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A DICTIONARY

OF

APPLIED CHEMISTRY

VOL. III.

A DICTIONARY OF APPLIED CHEMISTRY.

By T. E. Thorpe, B.Sc. (Vict.), Ph.D., F.R.S., Treas. C.S., Professor of Chemistry in the Normal School of Science and Royal School of Mines, South Kensington. Assisted by Eminent Contributors. 3 vols. 8vo. Vols. I. and II. 42*s.* each ; Vol. III. 63*s.*

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BY

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ASSISTED BY EMINENT CONTRIBUTORS

IN THREE VOLUMES

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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

A.	Liebig's Annalen der Chemie.
A. a.	Annales Agronomiques.
A. Ch.	Annales de Chimie et de Physique.
P. Am. A.	Proceedings of the American Academy of Arts and Sciences.
Am.	American Chemical Journal.
Ann. M.	Annales des Mines.
Am. S.	American Journal of Science.
A. C. J.	Journal of the American Chemical Society.
Am. Ch.	American Chemist.
Am. J. Pharm.	American Journal of Pharmacy.
An.	The Analyst.
Ar. N.	Archives néerlandaises.
Ar. Ph.	Archiv der Pharmacie.
B.	Berichte der deutschen chemischen Gesellschaft.
Bl.	Bulletin de la Société chimique de Paris.
B. B.	Berliner Akademie-Berichte.
B. C.	Biedermann's Centralblatt für Agricultur-Chemie.
B. J.	Berzelius' Jahresberichte.
B. M.	Berliner Monatsberichte.
Bentl. a. T.	Bentley and Trimen. Medicinal Plants.
Bl. Ph.	Bulletin de Pharmacie.
C. S. Mem.	Memoirs of the Chemical Society of London.
C. J.	Journal of the Chemical Society of London.
C. J. Proc.	Proceedings of the Chemical Society of London.
C. N.	Chemical News.
C. R.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences —Paris.
C. C.	Chemisches Central-Blatt.
D. P. J.	Dingler's polytechnisches Journal.
Fl. a. H.	Flückiger and Hanbury. Pharmacographia 2nd Ed.
Fr.	Fresenius' Zeitschrift für analytische Chemie.
J.	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
J. A.	Jahresbericht der Agrikultur-Chemie.
J. C. T.	Jahresbericht für Chemische Technologie.
J. M.	Jahrbuch für Mineralogie.
J. Ph.	Journal de Pharmacie et de Chimie.
J. pr.	Journal für praktische Chemie.
L. V.	Landwirthschaftliche Versuchs-Stationen.
M.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
M. S.	Le Moniteur Scientifique.
N. J. P.	Neuer Jahresbericht der Pharmacie.
N. R. P.	Neues Repertorium für die Pharmacie.
N. J. T.	Neues Journal von Trommsdorf.
P. M.	Philosophical Magazine.
P.	Poggendorff's Annalen der Physik und Chemie.
Ph.	Pharmaceutical Journal and Transactions.
Ph. C.	Pharmaceutisches Central-Blatt.
Ph. Centh.	Pharmaceutische Centralhalle.
Pr.	Proceedings of the Royal Society.
P. R. I.	Proceedings of the Royal Institution of Great Britain.
R. P.	Repertorium für die Pharmacie.
S. C. I.	Journal of the Society of Chemical Industry.
Sitz. B. or *Sitz. W.*	Sitzungsberichte der K. Akademie zu Wien.
Tr.	Transactions of the Royal Society.
U.	Ure's Dictionary of Arts, Manufactures and Mines. 7th Ed.
W.	Wiedemann's Annalen der Physik und Chemie.
W. J.	Wagner's Jahresbericht.
Z.	Zeitschrift für Chemie.

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OAK-BARK. The oak tree is generally barked from the beginning of May till the middle of July. The barkers make a longitudinal incision with a mallet furnished with a sharp edge, and a peculiar incision by means of a barking-bill. The bark is then removed by peeling-irons, the separation being promoted, when necessary, by beating the bark. It is stacked in pieces about 2 feet long (Ure), *v.* LEATHER.

OAK-GALLS *v.* GALL NUTS.

OAK-VARNISH *v.* VARNISH.

OATS *v.* CEREALS.

OBREGUIN. A substance intermediate in character between the fats and resins, occurring in Mexico on the twigs of *Alcea rosea.* Nearly insoluble in water; easily soluble in ether, chloroform, and turpentine oil. On evaporating, its solutions form a colourless, odourless mass, of the consistency of turpentine. Saponifiable by alkalis.

OBSIDIAN. A vitreous, volcanic rock, generally jet-black or of dark bottle-green tint, and nearly opaque, except on the thin edges, which are translucent. Obsidian results from the rapid cooling of rocks of acid type, such as trachytes, the corresponding glass in the basic series being termed *tachylite.* Microscopic examination of obsidian usually reveals the presence of numerous inclosures, known as crystallites and microlites, which may be so abundant as to render the rock opaque and devitrified. Many obsidians present a banded structure, while others are spherulitic. It is commonly said that pumice-stone represents the froth of a molten obsidian, but J. F. Blake, after examining the pumice workings at the Campi Bianchi in the Island of Lipari, believes, on the contrary, that obsidian is there formed by the fusion of a pumiceous rock (Proc. Geol. Assoc. 11, 1889, 173). Obsidian, when fractured, presents a sharp-cutting edge, and hence in parts of Mexico where the material is abundant, as at the Cerro de Navajas ('Hill of Knives'), it was used by the Aztecs for knives, razors, and arrow-heads. It has also been employed by savages in other volcanic countries as a kind of natural glass. Obsidian has occasionally been cut and polished as a gem-stone, but displays too little colour, even when thin, and is, moreover, too soft for general use. A dark variety with a silvery sheen is, however, used for ornamental purposes in Siberia, while a brownish-red streaked variety, known as 'mahogany-obsidian,' has been employed to a limited extent as a decorative material in the United States. On Obsidian Cliff, Yellowstone National Park, *v.* J. P. Iddings, Seventh Ann. Rep. U.S. Geol. Sur. 1888. F. W. R.

OCCLUSION (*occludo*, to shut up). Graham's term for the process of absorption or condensation of gases within the pores of a substance, *e.g.* the absorption of hydrogen by platinum and palladium, or the condensation of marsh-gas or fire-damp in coal.

OCHRE. A name applied to various native pigments, distinguished according to colour as yellow, brown, and red ochres, and consisting essentially of ferric hydrate, usually more or less earthy by admixture with clay or sand. Deposits of fine yellow ochre occur in the Lower Greensand of Shotover Hill, near Oxford. Red and brown ochres are commonly associated with iron-ores, especially with the hæmatite occurring in pockets in the carboniferous limestone, and have been worked in South Wales, the Forest of Dean, near Bristol, at Brixham in Devonshire, Ulverston in Lancashire, and near Workington in Cumberland. Some of the finest ochres of commerce are obtained from France, and are known as Auxerre and Rochelle ochres. In the United States ochres are worked in connection with many deposits of iron-ore, especially in Virginia and Pennsylvania. Some ochres are so pure as to be ready for use after having been simply dried, ground, and bolted; while others require careful preparation by washing and levigating. The value of an ochre depends, not only on its colour, but on the proportion of oil required to be mixed with it for use as a pigment. The presence of finely-divided silica is not always detrimental to an ochre, inasmuch as it may enable the paint to adhere to fibres of the wood to which it is applied, and by filling up spaces may improve its covering power. Coarse ochre is extensively employed in the manufacture of oilcloth and linoleum, while the finer kinds of ochre are valued by the papermaker for staining the pulp to its required tint. In commerce the term 'ochre' is frequently restricted to the pale yellowish-brown varieties. In mineralogy, on the contrary, it is extended to a variety of metallic oxides and other compounds formed as products of alteration and occurring as earthy incrustations on the minerals from which they have been derived by atmospheric action. Thus the mineralogist recognises such bodies as antimony ochre, bismuth ochre, molybdic ochre, nickel ochre (an arseniate), uranium ochre (a sulphate), and wolfram ochre. F. W. R.

OCHROITE *v. Cerium metals.*

OCRE DE RU. *Brown ochre v.* PIGMENTS.

OCTOIC ACID. *Caprylic acid v.* FATTY ACIDS.

OCTYL *Capryl* C_8H_{17}. The eighth alcohol-radicle of the series C_nH_{2n+1}. Like other members of this series, it cannot exist in the free state; when liberated from its compounds it is converted into dioctyl $C_{16}H_{34}$, a body isomeric and perhaps identical with hydride of cetyl.

The compounds of this radicle occur in petroleum, in the seeds of the common- and cow-parsnip, and in the products of the distillation of some varieties of coal.

OCTYLIC ALCOHOL $C_8H_{17}.OH$. A large number of isomeric alcohols with this formula are possible, but only the following have been prepared:—

Primary alcohols. *Iso-heptyl carbinol* $CH.Me_2.C_5H_{10}OH$. B.p. 194·1° (cor.) (Gartenmeister, A. 233, 249). 195·5° (in the vapour) (Zander, A. 224, 84). Sp.gr. $\frac{0}{0}$ = ·8369 (Gartenmeister), $\underline{0}$ = ·8375 (Zander).

Properties.—A colourless oily fluid, with a penetrating aromatic odour. The taste is sweetish at first, then pungent and burning. It is miscible with alcohol and ether, but nearly insoluble in water.

Occurrence.—In the free state, and as acetate and caproate in the seed of *Heracleum Sphondylium*, the cow-parsnip, and of *Heracleum giganteum* (Zincke, A. 152, 1; Moslinger, A. 185, 26); as octylic butyrate in the oil of the ripe seeds of *Pastinacea sativa*, the common parsnip (Renesse, A. 166, 80).

Preparation.—The portion of cow-parsnip oil which boils between 190°–195° is collected and purified by fractional distillation, the acetate passes over between 206°–208°, and is saponified and distilled to obtain the alcohol.

Reactions.—On oxidation octoic acid is formed.

Secondary alcohols. (1.) *Methyl-hexyl carbinol* $(CH_2)_3Pr^{\beta}.CHOH.Me$. B.p. 179°–179·2° at 762 mm. (Schiff, A. 220, 103), 179·5° (Schorlemmer, J. 1875, 28), 177·6°–177·8° at 745·4 mm. (Brühl, A. 203, 28). Sp.gr. $\frac{20}{4}$ = ·8193, $\frac{179}{4}$ = ·67815 (Brühl), $\underline{17}$ = ·823 (Bouis, A. 97, 34), $\underline{16}$ = ·826 (Pelouze and Cahours, A. Ch. 129, 91). Heat of combustion 1,262,105 cal. (Louguinine, A. Ch. [5] 25, 141).

Formation.—By the distillation of alkaline ricinoleates with excess of potash (Morchnin, A. 87, 111; Bouis, *loc. cit.*; Städeler, J. 1857, 358; Dachauer, A. 106, 269; Schorlemmer, A. 147, 222). By the distillation of the saponified oil of the seed of *Curcas purgans* (Silva, Z. 1869, 185).

Properties.—A limpid, oily, inactive liquid, with a strong aromatic odour, soluble in alcohol, ether, wood-spirit, and acetic acid, insoluble in water. It dissolves phosphorus, sulphur, iodine, fused zinc chloride, fats, resins, and copals.

Preparation.—Castor oil (which contains sodium ricinoleate) is distilled with excess of potash; the portion which passes over between 176°–180° is collected and purified by fractional distillation.

Reactions.—On oxidation it yields, first, methyl-hexyl ketone $MeCOC_6H_{13}$, subsequently acetic and normal caproic acids are formed. It reduces oxide (but not nitrate) of silver when heated with it, forming a metallic mirror. With hydrochloric acid, phosphorus pentachloride, bromine or iodine and phosphorus, &c., it exhibits the usual reactions of secondary alcohols.

(2.) Pelouze and Cahours (J. 1863, 528) obtained a secondary octyl alcohol by distilling octyl acetate from American petroleum with potash. B.p. 180°–184°. It is perhaps identical with methyl-hexyl carbinol.

(3.) **Octylene hydrate.** B.p. 174°–178°. Sp.gr. $\underline{0}$ = ·811 (Clermont, J. 1868, 449).

Properties.—A mobile, limpid liquid, with an aromatic smell and pungent taste, soluble in alcohol or ether, but not in water.

Preparation.—By the distillation of octylene acetate with anhydrous potash.

Reactions.—On oxidation it yields acetic and caproic acids and a ketone.

(4.) $Et_2CH.CHOH.Et$. B.p. 164°–166° (Wingradow, A. 191, 125).

Properties.—A clear liquid, with a pleasant odour. Scarcely soluble in water, combines with hydrogen iodide on warming.

Preparation.—Zinc ethyl and bromacetyl-bromide are mixed at a low temperature, in the proportion of 3 molecules of the former to one of the latter, allowed to stand for some time, and distilled.

(5.) **Ethyl-isoamyl carbinol** $Pr^{\beta}(CH_2)_2.Et.CHOH$. B.p. 182°–186° (Schorlemmer, A. 152, 152).

Preparation.—The octane produced by the action of zinc and hydrochloric acid on the secondary octyl iodide prepared from methyl-hexyl carbinol is converted into acetate, and distilled with alcoholic potash.

Reactions.—On oxidation with chromic acid it yields an acid isomeric with caprylic acid $C_8H_{16}O_2$, and a ketone isomeric with methyl-hexyl ketone, but which on further oxidation splits up into propionic and valeric acids, without a trace of acetic acid.

(6.) **Diisobutyl hydrate.** (a.) *Primary alcohol.* B.p. 179°–180° at 765 mm. (uncor.), remains fluid at −17°, sp.gr. $\frac{0}{4}$ = ·841, $\frac{20}{4}$ = ·828, $\frac{100}{4}$ = ·767. V.D. = 66·02 (calculated 65·0) (Williams, C. S. Mem. 35, 125).

Preparation.—By saponification of the acetate with potash and fractional distillation.

Properties.—A clear liquid, with an orange-like odour and a burning taste, soluble in alcohol and ether.

(b.) *Isosecondary alcohol.* This is obtained together with the primary alcohol, and separated from it by fractional distillation. B.p. 160°–163° under 755 mm. Sp.gr. $\frac{15^{\circ}}{4^{\circ}}$ = ·820. $\frac{30^{\circ}}{4^{\circ}}$ = ·811. V.D. = 65·38 (calculated 65·38) (Williams, *loc. cit.*).

Tertiary alcohols. (1.) *Diethylpropylcarbinol.* $Et_2.CPr.OH$. B.p. 145°–155° (Butlerow, Bl. 5, 17).

Preparation.—Butyrylchloride C_3H_7COCl is treated with zinc ethyl. The product is left for several days till it becomes viscid; it is then heated, acidified with hydrochloric acid, and distilled.

Properties.—A viscid liquid, with an alcoholic camphorated odour, lighter than water, and slightly soluble in it.

Reactions.—By oxidation with chromic acid, propionic and acetic acids are formed.

(2.) *Isodibutol* $Me_3.C.CH_2.CMe_2OH$. B.p. 146·5–147·5°. Sp.gr. $\frac{0}{0}$ = ·8417, congeals at − 20°. A colourless viscid liquid, with a musty camphorated odour.

Preparation.—From di-isobutylene hydriodide and silver oxide.

Reactions.—On oxidation it yields acetone, trimethylacetic acid, acetic acid, an octoic acid $C_8H_{16}O_2$, and a ketone $C_7H_{14}O$ (Butlerow, A. 189, 53).

OCTANE. *Octyl hydride, Capryl hydride* C_8H_{18}. This hydrocarbon is one of the constituents of American petroleum, and is found in the portion of the oil boiling between 115° and 130°. Ligroïn consists essentially of C_7H_{16} and C_8H_{18} (Pelouze and Cahours, A. 127, 197). It is also found among the light oils obtained by distilling Wigan cannel coal at a low temperature (Schorlemmer, C. S. 15, 419).

Eighteen isomeric hydrocarbons, having the formula C_8H_{18}, are theoretically possible, but only a few of these have been prepared. The octane from American petroleum may be separated by prolonged distillation into two hydrocarbons, one of which boils between 119°–122°, the other between 123°–125°.

(1.) **Octyl hydride.** B.p. 125·46° (cor.) (Thorpe, C. S. Mem. 37, 217); 124° (Schorlemmer, A. 161, 281). Sp.gr. $\frac{0}{4}$ = ·71883 (Thorpe); $\frac{17}{}$ = ·7032 (Schorlemmer). V.D. = 56·68 (calculated 56·88).

Formation.—By the action of Zn and HCl on secondary octyl iodide (Schorlemmer, A. 152, 152); by heating sebacic acid with baryta (Riche, A. 117, 265); by the action of sodium on normal butyl iodide (Schorlemmer); by the action of sodium amalgam on isoprimary octyl iodide (Zincke, A. 152, 15); by the action of zinc chloride on amylic alcohol (Würtz, A. 128, 230); by the dry distillation of the lime soap of Menhaden oil; by passing tridecane $C_{13}H_{26}$ through a red-hot tube (Vohl, J. 1865, 841); also by heating phthalic acid, indigo blue, or acenaphthen, &c., with hydrogen iodide.

Properties.—It is a colourless liquid, with a faint ethereal odour, exhibiting the general characteristics of the paraffins. The octanes prepared by the above methods are probably not all identical, but in physical and chemical characters they are almost undistinguishable.

Diisobutyl $Me_2CH(CH_2)_2CHMe_2$. B.p. 108·53° (cor.) (Thorpe, *loc. cit.*); 108°–108·3° at 745 mm. (Williams, C. J. 35, 125); 107·8°–107·9° (Schiff, A. 220, 88). Sp.gr. $\frac{0}{4}$ = ·7111 (Thorpe); $\frac{12·1}{4}$ = ·7001; $\frac{107·8}{4}$ = ·6166 (Schiff). V.D. = 56·90. (calculated 56·88) (Thorpe). Critical temperature 270·8 (Pawlewski, B. 16, 2634). Capillarity constant at boiling-point. $a^2 = 3·909$ (Schiff, A. 223, 104). $\mu_D = 1·3943, \frac{\mu_D - 1}{\alpha} = ·5655, \alpha = 0·6972$ at 16°. Refraction equivalent $\frac{P\mu_D - 1}{\alpha} = 64·47$.

Preparation.—By the action of sodium on isobutyl iodide (Würtz, A. 96, 365); by the action of sodium on isoamyl and isopropyl iodides (Schorlemmer, A. 144, 188); by the electrolysis of potassium valerate.

Properties.—A colourless, mobile liquid, with an ethereal odour and burning taste.

Reactions.—On oxidation with chromic acid, acetic acid and carbonic anhydride are formed.

On chlorination by Schorlemmer's method (Phil. Trans. 1872, 122) a mixture of primary and secondary chlorides is obtained. Similarly, a mixture of primary and secondary acetates is formed by the action of glacial acetic acid and potassium acetate (Williams, C. J. 35, 125).

Hexmethyl ethane CMe_3CMe_3. A crystalline substance, m.p. 96°–97°. B.p. 105°–106° (Lwow and Chrapowicki, Bl. 35, 169). Obtained by the action of sodium on tertiary-butyl iodide.

OCTYL CHLORIDES $C_8H_{17}Cl$.

Iso-primary chloride. From isoheptylcarbinol. B.p. 179·5°–180°. Sp.gr. $\frac{16}{}$ = ·8802.

Preparation.—By the action of hydrochloric acid gas on isoheptyl carbinol (Zincke, *loc. cit.*). A limpid liquid, soluble in absolute alcohol and in ether, insoluble in water.

Secondary chlorides. (1.) From *methylhexyl carbinol.* $C_6H_{13}.CHCl.Me$. B.p. 175° (Bouis), 170°–172° (Schorlemmer, C. J. 15, 419), 168°–172° (Pelouze and Cahours, A. 129, 91). Sp.gr. $\frac{18}{}$ = ·892 (Schorlemmer), $\frac{16}{}$ = ·895 (Pelouze and Cahours).

Formation.—By the action of hydrogen or phosphoric chloride on the carbinol (Bouis); by the action of hydrogen chloride on octylene (Berthelot, A. 104, 185); by the action of chlorine on octane (Schorlemmer; Würtz, J. 1863, 509; Pelouze and Cahours).

Properties.—A colourless liquid, with a strong smell of oranges.

Reactions.—It does not precipitate salts of silver. It is decomposed by potassium or sodium in the cold, yielding dioctyl $C_{16}H_{34}$. By repeated distillation with sodium, hydrogen is evolved and octylene C_8H_{16} is formed.

(2.) The octyl chloride prepared from petroleum octane exhibits the same reactions as that obtained from the alcohol, but on treatment with concentrated acetic acid and potassium acetate, octylene and octylacetate are formed in equal quantities, whereas the chloride from the carbinol yields three times as much octylene as octyl acetate (Schorlemmer, A. 152, 152).

(3.) **Diisobutyl chloride.** B.p. 165°. Sp.gr. $\frac{10·5}{}$ = ·8834 (Schorlemmer, A. 144, 190).

Tertiary chlorides. (1.) From *diethylpropylcarbinol* $Et_2.PrCHCl$. B.p. 155°. A liquid with a peculiar unpleasant odour. Prepared by the action of phosphoric chloride on the carbinol (Butlerow, Bl. 5, 17).

(2.) **Isodibutol chloride** $Me_3.C.CH_2.CClMe_2$. Boils with decomposition at 145°–150°. Sp.gr. $\underline{0}$ = ·890. It is formed by the action of fuming hydrochloric acid on diisobutylene at 100° (Butlerow, A. 189, 51).

Octyl bromides.

(1.) *Primary* $C_7H_{15}.CH_2Br$. B.p. 198°–200°. Sp.gr. $\underline{16}$ = 1·116. A colourless liquid prepared by the action of bromine and phosphorus on normal octyl alcohol.

(2.) *Secondary* $C_6H_{13}.CHBr.Me$. B.p. 187·5°–188·5° at 741 mm. Sp.g. $\underline{22}$ = 1·0989 (Lachowicz, A. 220, 185).

Preparation.—By treating methylhexylcarbinol with bromine and phosphorus, or by saturating the carbinol with hydrogen bromide at 0°, and heating for a few hours to 100°.

Properties.—It is an oily liquid, resembling the chloride in smell; it is soluble in alcohol but not in water. It boils with decomposition and leaves a carbonaceous residue when distilled. It precipitates silver salts in alcoholic solution, but less readily than the iodide.

Octyl iodides.

Primary iodide $C_7H_{15}.CH_2I$. B.p. 220°–222°. Sp.gr. $\underline{16}$ = 1·338 (Zincke, A. 152, 1).

Preparation.—By the action of iodine and phosphorus or of hydrogen iodide on the alcohol (Möslinger, A. 185, 55). It is a colourless liquid which reddens on warming; it is soluble in absolute alcohol or in ether, but insoluble in water (Zincke).

Secondary iodides. (1.) From methylhexylcarbinol $Me.C_6H_{13}CHI$. It boils with decomposition at 211° (Bouis, A. Ch. 44, 131); 193° (Squire, C. J. 7, 108).

Preparation.—By the action of iodine and phosphorus on the carbinol. It is an oily liquid with an odour of oranges, reddens on exposure to light. With Na or K it behaves like the chloride. When heated with mercury, mercurous iodide, octylene, and free hydrogen are formed. The alcoholic solution precipitates silver salts.

(2.) *Octylene hydriodide.* B.p. 120°. Sp.gr. $\underline{0}$ = 1·33. $\underline{21}$ = 1·314. An amber-yellow liquid insoluble in water; it is decomposed by light, and by the action of mercury in the cold.

Tertiary iodide. *Isodibutol iodide* $Me_3.C.CH_2.CIMe_2$ is formed by the action of hydriodic acid on diisobutylene. It is decomposed by water (Butlerow, A. 189, 52).

Octyl ethers. *Isoprimary octyl oxide.* From isoheptyl carbinol. B.p. 280°–282°. Sp.gr. $\underline{17}$ = ·8050. An oily liquid easily soluble in hot alcohol or ether. It is prepared by the action of sodium octylate on the isoprimary iodide (Möslinger, A. 185, 57).

Mixed ethers. *Ethyl-octyl oxide.* B.p. 182°–184°. Sp.gr. $\underline{17}$ = ·794. A colourless mobile liquid with a pleasant ethereal smell; soluble in alcohol and ether but not in water. It is prepared from sodium octylate and ethyl iodide.

Secondary ether. From methylhexylcarbinol.

Preparation.—By distilling sodium octylate with chloride or bromide of octyl, or by distilling the secondary alcohol (from castor oil) with sulphuric acid (Chapman, C. J. 18, 290).

Mixed ethers. *Ethyl octyl ether* $C_8H_{17}.O.Et$. B.p. 177°. Sp.gr. $\underline{16}$ = ·791. V.D. = 5·1. *Methyl octyl ether* $Me.O.C_8H_{17}$. B.p. 160°–161°. Sp.gr. $\underline{16}$ = ·83. *Amyl octyl ether* $C_8H_{17}O.C_5H_{11}$. B.p. 220°. Sp.gr. $\underline{20}$ = ·608. These are colourless mobile liquids, soluble in alcohol and ether but not in water, prepared by the action of the iodides of the radicles on sodium octylate (Wills, J. 1853, 509).

Octyl sulphides. (1.) *Primary sulphide* $(C_8H_{17})_2S$. Boils with decomposition over 310°. Sp.gr. $\frac{17}{17}$ = ·8419. A faintly-yellow mobile liquid soluble in warm alcohol, and miscible with ether. It is prepared by the action of an alcoholic solution of potassium sulphide on primary octyl chloride. Sulphuric acid forms with it a white amorphous mass probably of *Octyl sulphon* $(C_8H_{17})_2SO_2$; mercuric chloride gives crystalline needles of $C_8H_{17}S.HgCl_2$. It forms no compound with the alcoholic iodides.

(2.) *Secondary sulphide.* An oily liquid lighter than water and having an unpleasant odour. It is prepared by heating an alcoholic solution of sodium sulphide with secondary octyl iodide till the mixture becomes turbid, and then allowing the sulphide to separate out. It is slightly soluble in alcohol and decomposes on heating.

Methyl hexyl ketone $C_6H_{13}.CH_3.CO$. A liquid with an aromatic odour. B.p. 171°. Sp.gr. $\underline{17}$ = 0·817. It is obtained as a by-product in the preparation of the alcohol, also by the oxidation of the alcohol, and by the distillation of a mixture of calcium œnanthylate and calcium acetate (Staedler, J. Pr. 72, 241). On oxidation it yields acetic and caproic acids. With the acid sulphites of the alkaline metals it forms compounds which crystallise in pearly scales.

Ethereal salts of primary octyl. The following constants have been determined by Gartenmeister (A. 233, 249):—

	B.p. °	Sp.gr. $\frac{0}{0}$	Sp.gr. $\frac{\text{B.p.}}{0}$	Ratio of vol. at b.p. to vol. at 0°	Specific volume
Formate	198·1	0·8929	0·7156	1·2477	220·3
Acetate	210·0	0·8847	0·6981	1·2672	245·6
Propionate	226·4	0·8833	0·6860	1·2876	270·5
Butyrate	242·2	0·8794	0·6751	1·3028	295·6
Valerate	260·2	0·8784	0·6618	1·3272	322·6
Caproate	275·2	0·8748	0·6509	1·3440	349·6
Heptoate	290·4	0·8757	0·6419	1·3651	376·2
Octoate	305·9	0·8755	0·6318	1·3858	404·3

These bodies are all colourless liquids soluble in or miscible with alcohol and ether. The first six are prepared by the action of the silver salts of the acids on the bromides or iodides of octyl. The heptoate is prepared by the action of sulphuric and heptoic acids on octyl alcohol. The octoate is obtained as a by-product in the oxidation of octyl alcohol.

Octylic acetate occurs naturally in the ethereal oil of *Heracleum Sphondylium*; it is a mobile fluid with a pleasant odour of apples and a burning spicy taste. The butyrate occurs in the oil of the seeds of *Pastinacea sativa*.

Octyl acetoacetate $C_{14}C_{26}O_3$. B.p. 280°–282° (not cor.). Sp.gr. $\frac{18\cdot5°}{17\cdot5°}$ = ·9354. A clear, highly refractive liquid, obtained by the action of sodium acetoacetate on octyl iodide. It decomposes on saponification into octyl acetone and octyl acetic acid.

Octyl benzoate $C_8H_{17}.O.C_6H_5CO$. B.p. 305°–306°. A colourless liquid with a weak aromatic odour easily soluble in alcohol and ether (Zincke, A. 152, 1).

Octyl sulphuric acid is prepared from concentrated sulphuric acid and octyl alcohol. The barium salt $Ba(C_8H_{17}SO_4)_2$ forms large anhydrous nacreous plates very slightly soluble in hot water and alcohol. The potassium salt $KC_8H_{17}SO_4$ forms a white soluble semi-crystalline mass with a soapy feel.

Octyl nitrite. B.p. 175°–177°. Sp.gr. $\frac{17^\circ}{} =$ ·862. Obtained by heating octyl alcohol saturated with nitrous acid to 100° (Eichler, B. 12, 1887).

Octyl allophanate $NH_2CO.NH.COOC_8H_{17}$. Shining needles melting at 155°–160°, soluble in hot alcohol. Obtained by the action of chloroformamide on the alcohol.

Ethereal salts of secondary octyl. From methyl hexyl carbinol.

Octyl acetate B.p. 193° (Bouis, A. 44, 135); 191°–192° (Dachauer, A. 106, 269). A mobile liquid with a pleasant fruity odour, lighter than water, soluble in alcohol and ether, and also without change in not too concentrated sulphuric acid. It is easily saponified by potash. It is prepared (1) by the action of acetic acid or of an alkaline acetate and sulphuric acid upon the secondary alcohol; (2) by the action of silver or potassium acetate on the haloid compounds of the secondary alcohol; (3) by the action of acetyl chloride on sodium octylate.

The *monochloracetate* is prepared by passing hydrogen chloride into a mixture of the alcohol and acetic acid. B.p. 234°. Sp.gr. $\frac{10^\circ}{} =$ ·9904. It is a colourless neutral mobile oil with an ethereal odour and burning taste. It is soluble in alcohol and ether.

The *di-* and *tri-chloracetates* are obtained together with the monochloracetate. The former boils at 244°, the latter at 266°. They are colourless ethereal oils, lighter than water (Gehring, C. R. 104, 1000).

Octyl nitrate $NO_3CHC_6H_{13}CH_3$. A liquid with a pleasant smell resembling acetic ether. It begins to boil at 80° but soon decomposes. It is lighter than water, is soluble in alcohol, and is prepared by the action of silver nitrate on octyl iodide in alcoholic solution (Bouis).

Octyl nitrite $C_8H_{17}O.NO$. A dark-yellow mobile liquid. B.p. 165°–166°. Sp.gr. $\frac{0}{} =$ ·881. Obtained by the action of glyceryl trinitrite on the alcohol. It is soluble in ether and chloroform, and is decomposed by acids and by alcohol (Bertoni, C. C. 1887, 35).

Octyl sulphuric acid is obtained by the action of concentrated fuming sulphuric acid on octyl alcohol. It is a colourless syrupy strongly acid liquid, easily soluble in water and alcohol; the diluted acid is decomposed on boiling into secondary octylic alcohol and sulphuric acid. It dissolves iron, zinc, &c., with evolution of hydrogen, and completely neutralises the bases.

The *barium salt* forms flexible nacreous plates containing three molecules of water on separating from a hot solution, or mammillary aggregations with two molecules of water on evaporating in a vacuum. It is soluble in water and alcohol, and has at first a bitter, then a sweet taste. It turns red on standing, blackens at 100°, and decomposes without melting.

The *calcium salt* forms white laminæ with a soapy feel and bitter taste.

The *potassium salt* $K.C_8H_{17}SO_4 + \frac{1}{2}OH_2$ forms white shining plates with a greasy feel; the taste is at first bitter, then sweet. It is soluble in water and alcohol, reddens and is decomposed at 100°.

Octyl phosphoric acid is formed by digesting octyl alcohol with glacial phosphoric acid. It forms soluble salts with lead or barium (Bouis).

Octylic palmitate and stearate are formed by prolonged heating of the alcohol with the respective acids to 200°. The palmitate melts at 8·5°, the stearate at −4·5° (Hanhort, C. R. 47, 230).

Octyl carbamate is formed by the action of cyanogen chloride on the alcohol. B.p. 135° (under 20 mm. pressure). It is very soluble in alcohol, from which it separates out in colourless crystals melting at 54°–55°. At ordinary pressures it boils with decomposition at 230°–232°, with partial conversion into cyanuric acid.

Octyl thiocyanate $C_8H_{17}.S.CN$. B.p. 142° is formed by the action of KCNS on the secondary iodide.

Octyl thiocarbimide $C_8H_{17}{-}N{=}CS$. A colourless liquid. B.p. 234°, formed by Hofmann's reaction from octylamine.

Octyl thiosinnamine $C_8H_{17}.NH.CSNH_2$. B.p. 112·5°, formed by the action of ammonia on the preceding compound. It is soluble in alcohol and ether, and separates out from its solution in colourless laminæ (Jahn, B. 8, 803).

OCTYLAMINES.

(1.) **Amines of primary octyl.** (*a*) *Monamines.* B.p. 185°–187° (Eichler, B. 12, 1885).

Preparation.—By the action of alcoholic ammonia upon octyl iodide at 100° (Renesse, A. 166, 85). By the action of iron filings and glacial acetic acid upon nitro-octane (Eichler). By heating the alcohol and $ZnCl_2.NH_3$ at 280° (Merz and Gasiorowski, B. 17, 629).

Properties.—The monamine is a colourless basic oil which takes up CO_2 from the air. In contact with water it forms white crystalline needles. With bromine and potash an oily compound $C_8H_{17}NBr_2$ is formed, which is converted on boiling into heptyl nitrile $C_7H_{17}CN$ (Hofmann, B. 17, 1920). The *hydrochloride* $C_8H_{19}N.HCl$ is easily soluble in water and alcohol; the *platinochloride* forms yellow plates soluble with difficulty in water or alcohol; the *picrate* $C_8H_{17}.NH_2.C_6H_3N_3O_7$ crystallises from alcohol in oblong tables melting at 112°–114°. A primary amine may also be prepared by heating pelargonamide with bromine and potash. B.p. 171°–174° (Hofmann, B. 15, 773).

(*b*) *Diamine* $(C_8H_{17})_2NH$. M.p. 36·05°. B.p. 297°–298°.

This body is produced together with the monamine by the action of alcoholic ammonia upon octyl iodide, or of $ZnCl_2.NH_3$ on octyl alcohol.

It crystallises in needles, soluble in alcohol or ether, and having a strong smell of tallow; the *hydrochloride* forms plates soluble in alcohol;

the *platinochloride* $(C_{16}H_{33}N.HCl)_2PtCl_4$ crystallises in small scales.

(*c*) *Triamine.* B.p. 365°–367°. Obtained by the same reactions as the mon- and di-amines, and separated from them by fractionation. It is an oil which slowly congeals to a white crystalline mass, and is very soluble in ether and absolute alcohol.

The *platinochloride* $(C_{24}H_{51}N.HCl)_2PtCl_4$, forms a brown oil which dries up to a sticky mass.

(2) **Amines of secondary octyl.**

(*a*) *Monamine.* B.p. 172°–175° (Pelouze and Cahours), A. 92, 399, 175° (Bouis, A. Ch. 44, 139), 164° (Squire, C. J. 7, 108), 162·5° (Jahn, M. 3, 172). Sp.gr. = ·786 (Squire).

Preparation.—1. By heating chloride or iodide of the secondary octyl with alcoholic ammonia.—2. By the saponification of the distillate of a mixture of octyl sulphate and potassium cyanate.—3. By the action of $ZnCl_2.NH_3$ upon methyl hexyl carbinol at 280°.

Properties.—It is a colourless, bitter, very caustic inflammable liquid with an ammoniacal fishy odour. It is insoluble in water, but precipitates metallic salts and dissolves silver chloride. On heating with secondary octyl iodide, ammonium iodide, octylene, polyoctylene, and iodide of secondary octylamine are formed (Jahn, *loc. cit.*). The *hydriodide* $C_8H_{20}NI$ forms large plates easily soluble in water; the *hydrochloride* $C_8H_{20}NCl$ is a very deliquescent solid which crystallises *in vacuo* in large nacreous plates; the *aurochloride* $C_8H_{20}NAuCl_4$ forms shining yellow laminæ resembling lead iodide. The *platinochloride* separates from boiling solutions in brilliant golden-yellow scales soluble in alcohol or ether.

Pelouze and Cahours (*loc. cit.*) obtained a monamine from petroleum-octane which they consider identical with the above.

(*b*) *Diamine* $(C_8H_{17})_2NH$. An oil with an aromatic odour, b.p. 260°–270°, obtained by the action of $ZnCl_2NH_3$ on methyl hexyl carbinol at 280°.

The *platinochloride* $(C_{16}H_{35}N.HCl)_2PtCl_4$ forms a brown mass; the *aurochloride* $C_{16}H_{35}NHClAuCl_3$ crystallises from alcohol in golden-yellow laminæ.

(*c*) *Triamine* $(C_8H_{17})_3N$; an aromatic oil boiling at 370°. It is prepared like the diamine. The *hydrochloride* is oily and soluble in alcohol; the *platinochloride* $(C_{24}H_{51}N.HCl)_2PtCl_4$ is a reddish-brown resin.

Primary octyl phosphine. B.p. 184°–187°. Sp.gr. $\frac{17}{} = \cdot 8209$. A limpid, mobile, highly refractive liquid, soluble in alcohol, ether, benzene, and glacial acetic acid. It is obtained by the action of phosphonium iodide and zinc oxide upon octyl iodide.

Nitric acid oxidises the solution in glacial acetic acid to octyl-phosphinic acid, an amorphous body soluble in hot acetic acid. Oxygen, bromine, and iodine act less energetically upon octyl phosphine than upon the phosphines of the lower members of the series. Fuming hydriodic acid forms *octyl phosphonium iodide* $PH_3C_8H_{17}I$, a semicrystalline mass which decomposes on standing, or on solution in ether or benzene.

Octonitrile $C_8H_{17}NO$. A yellow liquid boiling at 198°–200°, obtained by the action of bromine and potash on pelargonamide.

Octyl carbamine. B.p. 214°–216°. Sp.gr. $\frac{16}{} = \cdot 786$. Obtained by the action of potassium cyanide on octyl iodide. It is soluble in alcohol and ether.

Octoxylamide $C_7H_{15}CO.NH_2$, a crystalline mass melting between 105°–106°, prepared by treating octonitrile with concentrated sulphuric acid and very cold water. It is very slightly soluble in boiling water, and not at all in cold.

Nitro-octane. A liquid boiling at 205°–212°, obtained together with octyl nitrite by the action of silver nitrite on primary octyl iodide (Meyer, A. 171, 23).

Octyl nitrolic acid $C_8H_{16}NO.NO_2$. An oily body formed from nitro-octane, potash, potassium nitrite, and dilute sulphuric acid. Concentrated sulphuric acid decomposed it into octoic acid and nitrous oxide (Eichler, B. 12, 1885).

BENZENE DERIVATIVES OF PRIMARY OCTYL.

Octyl benzene. A colourless oil with a sweet taste. B.p. 261°–263° (uncor.); sp.gr. $\frac{15°}{15°} = \cdot 849$. B.p. = 262°–264°; sp.gr. $\frac{14}{} = \cdot 852$ (Ahrens, B. 19, 2717) (Schweinitz, B. 19, 640). It is obtained by the action of sodium on a mixture of brombenzene and octyl bromide in ethereal solution. It is miscible with alcohol, ether, or benzene.

Chloroctylbenzene $C_6H_4ClC_8H_{17}$ is a yellowish odourless oil soluble in alcohol and ether, b.p. 270°–275°. It is prepared by the action of chlorine and iodine on octylbenzene.

Bromoctylbenzene $C_8H_{17}.C_6H_4Br$, b.p. 285°–287°, resembles the chlorine derivative.

Moniodoctylbenzene. A yellow oil soluble in alcohol and ether, decomposes on distillation. It is obtained by treating octylbenzene (diluted with petroleum) with iodine and mercuric oxide.

Pariodoctylbenzene. A heavy oil, b.p. 318°–320°, prepared from amido-octylbenzene (*q. v.*) by the diazo- reaction. The corresponding derivative of the secondary alcohol (from castor oil) is a yellow oily liquid, b.p. 304°–305°. On oxidation with chromic acid both yield pariodobenzoic acid.

Metanitro-octylbenzene $NO_2.C_6H_4.C_8H_{17}$. Crystallises in long needles which melt at 123°–124° and sublime at a high temperature. It is prepared by the action of fuming nitric acid upon octylbenzene in the cold. It is slightly soluble in alcohol and chloroform. With potassium permanganate it yields metanitrobenzoic acid.

Orthonitro-octylbenzene, a thick yellow aromatic oil which decomposes at 100° and

Paranitro-octylbenzene which forms small yellow lustrous needles melting at 204°, and soluble in alcohol or ether, are found in the residue from the meta- compound.

Dinitro-octylbenzene, $C_8H_{17}.C_6H_3(NO_2)_2$ forms crystals melting at 226° but subliming below this temperature. It is soluble in alcohol and ether and is formed by the action of fuming nitric acid on the crystals of the meta- compound.

Orthamido-octylbenzenehydrochloride
$NH_2.C_6H_4.C_8H_{17}:HCl$.
Occurs in small lustrous white plates which redden on heating. It is formed by reducing the nitro- derivative with tin and hydrochloric acid (Ahrens, B. 19, 2717).

Paramido-octylbenzene, a colourless liquid, b.p. 310°–311°, volatilises in steam. It is obtained by the action of aniline hydrochloride, or of aniline and zinc chloride on primary octyl alcohol (from *Heracleum* oil). A similar derivative may be prepared from the secondary alcohol (from castor oil), b.p. 290°–292° (cor.).

Formylphenoctylamine $C_8H_{17}.C_6H_4.NH.CHO$ is obtained by the action of formic acid on amidoctylbenzene. It forms scales which melt at 35° and are soluble in alcohol or ether.

Acetylphenoctylamine $C_8H_{17}.C_6H_4NH.C_2H_3O$ is formed from amidoctylbenzene and acetic anhydride. It forms thin plates melting at 93°, and soluble in alcohol or ether.

Benzoylphenoctylamine $C_8H_{17}.C_6H_4.NHBz$ is obtained from amidoctylbenzene and benzoic chloride. It forms scales melting at 117° and soluble in alcohol or ether. The corresponding derivative of the secondary alcohol forms white needles melting at 109°.

Octylbenzoylnitrile is obtained by distilling formylphenoctylamine with zinc-dust. B.p. 312°. It is converted by oxidation into paroctylbenzoic acid.

Octylbenzene sulphonic acid. A thick syrupy strongly acid liquid formed by the action of Nordhausen acid on octylbenzene. Silver salt
$C_8H_{17}.C_6H_4.SO_3Ag.H_2O$.
Barium salt $(C_{14}H_{21}SO_3)_2Ba.H_2O$. Lead salt $(C_{14}H_{21}SO_3)_2Pb.3H_2O$ (Schweinitz, B. 19, 640).

Toluene derivatives of primary octyl.

Amido-octyltoluene (*Toloctylamine*)
$C_8H_{17}.C_6H_3Me.NH_2$
is prepared by treating the isoprimary alcohol with orthotoluidine and zinc chloride. It is a colourless oil which boils at 324°–326°, and forms a well-crystallised hydrochloride, sulphate, and oxalate.

Acetyltoloctylamine $C_8H_{17}.C_7H_6.NHAc$ forms slender white needles, m.p. 81°, soluble in alcohol and ether.

Benzoyltoloctylamine $C_8H_{17}.C_7H_6.NHBz$ forms lustrous scales, m.p. 117°, soluble in alcohol. These toluene derivatives are prepared in a manner analogous to the corresponding benzene derivatives.

Thiophen derivates of primary octyl.

Octylthiophen $C_8H_{17}.C_4H_3S$ is formed by the action of sodium on octyl bromide and iodothiophen, b.p. 257°–259°, sp.gr. $\frac{20·5}{20·5} = ·8118$. It is soluble in ether.

Bromoctylthiophen $C_4SH_2Br.C_8H_{17}$ boils at 285°–290° and solidifies at 5°.

Iodoctylthiophen $C_4SH_2I.C_8H_{17}$ is a yellow oil which solidifies at 0°. Sp.gr. $\frac{20°}{20°} = 1·2164$. Both the bromo- and iodo- compounds are prepared analogously to the corresponding benzene derivatives.

Octylacetothienone $C_8H_{17}.C_4SH_2.COMe$, an oil with a garlic-like odour, b.p. 350°–355°, and **Octyldiacetothienone** $C_8H_{17}.C_4SH(COMe)_2$, a yellow syrup, are prepared by the action of acetic chloride and aluminium chloride on octylthiophen.

Octylthiophencarboxylic acid
$C_8H_{17}.C_4SH(COOH)_2$
is obtained in microscopic needles melting at 185°, by the action of potassium permanganate on the diaceto- derivative. Barium, copper, and silver salts have been prepared.

Methyloctylthiophen
$C_8H_{17}.C_4SH_2Me[C_8H_{17}:Me = 2:5]$
is obtained by the action of sodium on iodothiotolen and octylic bromide. It is a colourless oil boiling at 270°, and on strongly cooling it solidifies to a crystalline mass which melts at 10°. The monobromo- derivative
$C_8H_{17}C_4SHMeBr$
melts at 20°.

OCUBA WAX *v.* Wax.

ODORINE. A volatile base found by Unverdorben in bone-oil. Probably impure picoline.

ŒNANTHIC ACID and **ŒNANTHIC ETHER.** According to Liebig and Pelouze (A. 19, 241), there is found in wine a small quantity of a body termed by them œnanthic ether. It is a very mobile liquid, with a strong vinous smell, and of a disagreeable taste; readily soluble in ether and alcohol, but very sparingly soluble in water. Is regarded by Delffs (A. 80, 290) as identical with ethyl pelargonate. This ether is now prepared commercially for flavouring common wines, brandy, &c., from the oxidised products of oil of rue (*v. Nonoic acids*, art. Fatty Acids). According to A. Fischer (A. 115, 247) the artificial product is a mixture of capric and caprylic acids. Many fusel oils contain both these acids, and amyl caprate is found in several Hungarian wines.

ŒNANTHOL, *Œnanthaldehyde, heptaldehyde, normal œnanthic*, or *Heptoic aldehyde*, $C_6H_{13}COH$, is one of the products of the dry distillation of alkaline ricinoleates and of the action of nitric acid on stearic and margaric acids.

The following method of preparation may be employed:—

Castor oil, which consists essentially of the glyceride of ricinoleic acid, is rapidly distilled until the residue becomes resinous, thus converting the greater part of the ricinoleic acid into œnanthol and hendecatoic acid:—

$$C_{18}H_{34}O_3 = C_6H_{13}COH + C_{11}H_{20}O_2.$$

The distillate is rectified, and the part coming over between 90° and 180° is shaken with a saturated solution of acid sodium sulphite, and is warmed and filtered. The mass of the double salt $C_6H_{13}COH.HNaSO_3H_2O$, separating out on cooling, is pressed between filter paper, mixed with a solution of sodium carbonate, and distilled in a current of steam. The œnanthol which floats on the distillate is separated and dried over anhydrous Glauber's salt or calcium chloride.

The yield of œnanthol is increased when the castor oil is distilled under reduced pressure.

Œnanthol is a highly refractive, very mobile, colourless liquid, of pungent aromatic smell, boiling at 154°, and having at 15° a specific gravity of 0·8231. It is slightly soluble in water, and dissolves in all proportions in alcohol and ether. Œnanthol rapidly oxidises on exposure to air. It reduces silver nitrate.

ŒNANTHYLIC ACID. *Heptoic acid v.* Fatty acids.

ŒNOCYANIN, the colouring matter of black grapes and red wines, is of colourless origin, and becomes blue through oxidation, and probably hydration, which may be shown by placing a green grape picked from a bunch which is just beginning to turn red in a vacuum of 1 to 2 mm. over boiled sulphuric acid for 3 or 4 days, or sufficient time to allow of the grape becoming hard and dry. The colour becomes yellow, but, on admitting air, moisture and oxygen are rapidly absorbed, the colour changing to blue black at the same time (Maumené, C. R. 95, 924).

ŒNOLIN. The name given to the natural red colouring matter of wine precipitable by lime or basic lead acetate. Is brown red whilst moist, but nearly black when dry, giving a violet red or brown-red powder, readily soluble in alcohol, and in water acidulated with vegetable acids. Is said to have the composition $C_{20}H_{20}O_{10}$, and to form a lead compound $C_{20}H_{18}PbO_{10}$ (Glénard, C. R. 47, 268; Varenne, Bl. [2] 29, 109). For the estimation of œnolin and œnotannin in wines *v.* F. Jean, C. R. 93, 966.

ŒNOMETER. A hydrometer designed for determining the alcoholic strength of wines.

OIL-GAS *v.* Gas, oil.

OIL, MINERAL, *v.* Petroleum.

OIL OF AMBER *v.* Oils, essential, and Resins.

OIL OF HARTSHORN *v.* Bone oil.

OIL OF VITRIOL *v.* Sulphuric acid.

OIL PULP *v. Aluminium oleates*, art. Aluminium.

OILS, ESSENTIAL, syn. *Essences.*

Volatile oils. The word oil appears to be derived from the Greek ἐλαία, the olive-tree (whence ἔλαιον, olive-oil or simply oil), through the Latin *oleum* and French *huile*. Hence it seems to have been originally applied to liquids which, like olive oil, are insoluble in water, combustible, and more or less viscid, and this may be regarded (save for a few unimportant exceptions, such as 'oil of vitriol') as the signification which the word has practically retained.

Two kinds of oil are recognised, namely, *Fixed* or *Fatty oils*, which will be dealt with in a separate article, and *Essential* or *Volatile oils*. The latter are distinguished from the former by the possession of strong and characteristic odours, and by being vaporisable without decomposition, and usually with little or no residue. A drop of olive or similar oil placed upon paper produces a translucent spot which does not disappear upon exposure to air, nor even when heated. A drop of essential oil, *e.g.* of lemon or of turpentine, also produces a translucent spot, but this stain soon disappears on free exposure to air. The composition of essential oils is various; many, like turpentine oil, consist of compounds of carbon and hydrogen only, others contain oxygen in addition to carbon and hydrogen, but their chemical constitution differs in different cases, the majority being ethereal salts or compound ethers, aldehydes, or phenols.

Many essential oils consist of hydrocarbons or other fluid bodies, mixed with solid oxidised compounds. When the latter are present in considerable amount, a portion usually separates out in a crystalline form by spontaneous evaporation of the more volatile liquid, or by exposure to cold. In such cases the solid is often referred to as the *stearoptene* (στέαρ, solid fat), whilst the liquid is called the *elæoptene*. The essential oils are almost all of vegetable origin. Some exist ready formed in vegetable tissues contained in cavities or glands which are often visible to the unaided eye, as in the leaves of mint, the rind of the orange, and in the fruits of the umbelliferæ. In a few cases the essential oil does not exist ready formed in the plant, but is a product, together with glucose and other substances, of the mutual action of chemical compounds which are present in the tissue, probably in distinct cells, and which react upon each other only in the presence of water. In the bitter almond, for example, there is no volatile oil, but only a fixed oil which may be obtained by simple expression. That the former is only produced when water is added may be proved by the fact that powdered bitter almonds have no characteristic odour till water has been added. Flour of mustard is also devoid of pungency until mixed with water.

The following are the chief methods of extraction:—

1. *Distillation of plants or parts of plants*, such as wood, leaves, flowers, or fruit, *with water.* Notwithstanding that nearly all essential oils boil at temperatures far above the boiling-point of water, these substances produce vapours of considerable tension, and these vapours have rather a high density at that temperature. Consequently, when a substance containing an essential oil is boiled with water, the escaping vapour is a mixture of water with a considerable, though relatively small, proportion of the oil.

The simplest application of this method consists in placing the vegetable matter in a copper or iron still provided with a worm, adding water, and keeping the fire under the still as long as the distillate presents a milky appearance. The residue in the still is then thrown away, and a fresh charge introduced. This is the plan adopted by the peasants in the south of France for the production of oil of wild rosemary upon the hill sides where the plant grows, and an equally simple plan is adopted in many herb distilleries.

Several modifications have been introduced of which the most important is the employment of steam as the source of heat instead of the naked fire. The capacity of the still used may vary up to 600 gallons or more. It is provided with an outer shell or jacket in which steam of 15 or 20 pounds' pressure is supplied. The still must also be provided with an agitator, which may be attached to a spindle passing through a stuffing-box below, and which may be kept in motion during the progress of the distillation so as to prevent the caking of solid matter upon the bottom of the still.

When the object of the process is to obtain essential oil only, and the water which distils over at the same time, and which is of course saturated with the oil, is not wanted, it is customary to return the latter to the still.

This may be done by reserving it after separation of the oil and employing it in place of pure water for the next charge. Another plan is to allow it to run back continuously into the still during the whole progress of the distillation.

This is most convenient in those cases in which the operation of extracting the oil is slow, and in which consequently a large quantity of the distilled water would otherwise accumulate.

In a few cases, such as clove, cinnamon, and sassafras, it is found advantageous to add a small quantity of common salt to the liquor in the still in order to raise the boiling-point.

The receiver employed is a vessel of cylindrical form having a tube at the side near the bottom rising vertically and terminating in a spout a little below the top of the receiver. A strainer is sometimes placed over the mouth to prevent splashing, and to keep out dirt. In this receiver the oil and water collect, the oil rising to the surface if its density is lower than that of water, whilst the latter flows away by the side tube leaving the oil in the receiver. On the other hand, if the oil is of greater density than water, it sinks and the water must be removed as it accumulates by means of a separate tap above.

2. *Distillation from semifluid exudation.*—Practically this process is applied to one case only, that of turpentine. The viscid resinous exudation collected from incisions made in the trees (for an account of the process see Flückiger and Hanbury, Pharmacographia) was formerly submitted to distillation without any addition, the volatile oil being collected in barrels and the residual resin drawn off while hot and fluid. According to Dr. Thomas F. Wood, of Wilmington, North Carolina, the following process is now employed: —' Turpentine is distilled in copper stills now. Formerly iron stills were used. All crude turpentine is distilled with water. A fifteen-barrel still (barrel weighs 280 lbs.) is charged early in the morning. Gentle heat is first applied until the mass is liquefied, and a coarse wire skimmer is used to remove the chips, bark, leaves, and such other foreign substances as rise to the surface, the temperature meanwhile rising until 316°F. is reached. All the accidental water (that contained in the crude turpentine as it comes from the forest) having been distilled off, a small stream of cold water is now let in, so that the heat is kept at or below 316°F., the boiling-point of oil of turpentine. The oil of turpentine and water now come over, and the mixture is caught in a wooden tub. The distiller tests the quality of the flow from time to time in a proof-glass, and the distillation is continued until the proportion of water coming over is nine of water to one of oil of turpentine. At this stage the heat is withdrawn, the still-cap is taken off, and the hot resin is drawn off by a valvular cock at the side of the still near the bottom. This resin passes through a strainer before it reaches the vat, to rid it of foreign substances which may not have been previously removed by the skimmer. The yield of oil of turpentine from " virgin dip " (the first exudation from a newly-boxed tree) is about five gallons to the barrel, about 20 per cent. being left in the resin, since the removal of a larger proportion would darken the colour, and consequently depreciate its value. The yield from " yellow dip " (the runnings of the second and subsequent years) is about four gallons to a barrel. The yield from " scrapings " (the inspissated gum from the tree facings) is about two to three and a half gallons according to age, and also to the proportion of trash which it contains.'

In extracting French turpentine from the produce of the district near Bordeaux the oil is frequently distilled off by blowing steam into the fluid contained in the still without the application of fire below. This method may be used with advantage in the case of many other substances containing essential oils, as distillation is effected very rapidly, and there is no risk of overheating the residue and getting products of decomposition mixed with the distillate.

3. *The process by the sponge and the écuelle.* In the case of the fruits of the orange tribe in which the oil glands are large and numerous, a portion of the essence can be extracted without distillation.

The following description of these processes has been given by D. Hanbury, F.R.S. (Pharmacographia) :—' The workman first cuts off the peel in *three* thick longitudinal slices, leaving the central pulp of a three-cornered shape with a little peel at either end. This central pulp he cuts transversely in the middle, throwing it on one side and the pieces of peel on the other. The latter are allowed to remain till the next day, and are then treated thus :—The workman seated holds in the palm of his left hand a flattish piece of sponge, wrapping it round his forefinger. With the other he places on the sponge one of the slices of peel, the outer surface downwards, and then presses the zest-side (which is uppermost) so as to give it for the moment a convex instead of a concave form. The vesicles are thus ruptured, and the oil which issues from them is received in the sponge with which they are in contact. Four or five squeezes are all the workman gives to each slice of peel, which done he throws it aside. Though each bit of peel has attached to it a small portion of pulp, the workman contrives to avoid pressing the latter. As the sponge gets saturated the workman wrings it forcibly, receiving its contents in a coarse earthen bowl provided with a spout; in this rude vessel, which is capable of holding at least three pints, the oil separates from the watery liquid which accompanies it, and is then decanted.

' The yield is stated to be very variable, 400 fruits affording nine to fourteen ounces of essence. The prisms of pulp and the exhausted pieces of peel are submitted to pressure in order to extract from them lemon juice, and are said to be also subjected to distillation. The foregoing is termed the *sponge-process* ; it is also applied to the orange. It appears rude and wasteful, but when honestly performed it yields an excellent product.

' Essence of lemon is prepared at Mentone and Nice by a different method. The object being to set free and to collect the oil contained in the vesicles of the peel, an apparatus is employed which may be thus described :—A stout saucer or shallow basin of pewter, about 8½ inches in diameter, with a lip on one side for convenience of pouring. Fixed in the bottom of this saucer are a number of stout, sharp, brass pins, standing up about half an inch; the centre of the bottom is deepened into a tube about an inch in diameter and five inches in length, closed at its lower end. This vessel, which is called an *écuelle à piquer*, has, therefore, some resemblance to a shallow, dish-shaped funnel, the tube of which is closed below.

'The workman takes a lemon in the hand, and rubs it over the sharp pins, turning it round so that the oil-vessels of the entire surface may be punctured. The essential oil which is thus liberated is received in the saucer, whence it flows down into the tube; and as this latter becomes filled, it is poured into another vessel that it may separate from the turbid aqueous liquid that accompanies it. It is finally filtered, and is then known as *Essence de Citron au zeste*. A small additional product is sometimes obtained by immersing the scarified lemons in warm water and separating the oil which floats off.

'A second kind of essence, termed *Essence de Citron distillée*, is obtained by rubbing the surface of fresh lemons, or of those which have been submitted to the process just described, on a coarse grater of tinned iron, by which the portion of peel richest in essential oil is removed. This grated peel is subjected to distillation with water and yields a colourless essence of very inferior fragrance, which is sold at a low price.'

4. *Expression.*—In a few cases (orange, lemon, &c.) a part of the essential oil may be obtained by submitting the material contained in bags, preferably of horsehair, to powerful hydraulic pressure.

5. *Maceration in fat.*—This process can hardly be reckoned among those by which essential oils are actually isolated, though it might be so employed. For the purposes of the perfumer it is necessary to avoid as much as possible the application of heat by which the fragrance of many natural essences is injuriously affected. In such cases as orange flower, rose, violet, and jonquil, a superior perfume is obtained by macerating the flowers in oil or in pure lard or paraffin melted by the heat of a water bath. The fat charged with the essence may afterwards be shaken up with alcohol which extracts a portion, the alcoholic solution being used in perfumery, the residual fat as a pomade.

6. *Enfleurage* or *absorption* is another process having the same object. In this case wooden frames (*châssis*) are used, having a glass bottom about 3 feet long by 2 feet wide and 3 inches deep. The glass bottom is covered with a layer of fat upon which the flowers (of jasmine, for instance) are sprinkled. A number of frames being placed in a pile are charged with fresh flowers every day or two till the fat is sufficiently perfumed.

The following list includes the more important essential oils met with in commerce. Except where otherwise stated it may be assumed that they are prepared from the plant by distillation with water or in steam.

The names used in pharmacy are generally added. The letters B. P. indicate that the oil is included in the British Pharmacopœia.

Abietene, from *Pinus Sabiniana* (of California), consists almost entirely of normal heptane $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$ (98·4°) (Thorpe, C. J. 1879, 1, 296) together with a little resin, possessing a smell of oranges. Used as a solvent of fats and in varnishes (Wenzell, Ph. [3] 2, 789).

Ajowan (*Thymol*, B. P.). From the fruit of an umbelliferous plant, *Carum Ajowan* (Benth. and Hooker) or *Ptychotis Ajowan* (D. C.), cultivated in India. Consists of a mixture of cymene $C_{10}H_{14}$ (176°) with 30 to 40 per cent. of thymol $C_{10}H_{14}O$ or $C_{10}H_{13}.OH = C_3H_7C_6H_3.OH.CH_3$ ($CH_3:OH:C_3H_7 = 1:3:4$), the latter crystallises readily from the oil on cooling it or evaporating at a low temperature. Thymol may also be extracted from the oil more completely by caustic soda, separating the aqueous solution and precipitating by hydrochloric acid. Thymol [50°] (230°) is only slightly soluble in water, but dissolves easily in alcohol, ether, glacial acetic acid, and solutions of alkalis. Used in medicine.

Almonds. *Oleum Amygdalæ amaræ.* The marc left after expression of the fixed oil is submitted to distillation with water. The essence results from the action of *emulsin*, a soluble nitrogenous ferment existing in both sweet and bitter almonds, upon *amygdaline*, a crystalline glucoside which occurs in bitter almonds only. The reaction is represented by the following equation:

$$\underset{\text{Amygdaline}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\substack{\text{Essential}\\\text{oil}}}{C_7H_6O} + \underset{\substack{\text{Hydro-}\\\text{cyanic}\\\text{acid}}}{HCN} + \underset{\substack{\text{Dextro-}\\\text{glucose}}}{2C_6H_{12}O_6}.$$

The yield of essential oil varies, partly according to the quality of the almonds, partly according to the proportion of sweet almonds intermixed with the bitter. From information supplied by Mr. C. Umney, who has had large experience in the distillation of essential oils, the marc yields on an average 1 per cent. of oil corresponding to about ½ per cent. from the original almonds.

The crude oil obtained by this process contains a mixture of benzoic aldehyde and hydrocyanic acid with phenyl-hydroxyacetonitril $C_6H_3.CH(OH)CN$, from which they are probably both formed, besides small quantities of benzoïn, $C_{14}H_{12}O_2$, &c. The oil can be freed from hydrocyanic acid by the following and other processes: (1) Redistillation from a mixture of lime and ferrous sulphate; (2) agitation with a strong solution of acid sodium sulphite, crystallisation of the double salt, and redistillation of the crystals with solution of soda; (3) boiling for a short time with strong hydrochloric acid, then diluting and distilling till the oil has passed over.

Pure essential oil of almonds is said to be more liable to oxidation upon exposure to air than the crude oil. If moist or mixed with spirit of wine it is rapidly converted into benzoic acid, but when carefully dried by immersing in it a lump of calcium chloride even the pure essence may be preserved almost indefinitely.

Benzaldehyde is also produced by the action of water upon the seeds and leaves of many plants of the orders *Amygdalaceæ* and *Pomaceæ*. At the present time a considerable quantity is manufactured from peach kernels.

Benzaldehyde may be obtained artificially by a number of chemical processes. It is manufactured for the use of the colour-maker, especially in making 'malachite green' by boiling benzyl chloride C_7H_7Cl (made from pure toluene) with lead nitrate and water. The pure essential oil can be prepared from the crude product by making first the compound with sodium acid sulphite and decomposing this with soda.

Purified essential oil of almonds is sometimes adulterated with spirit of wine, which is added with the object of disguising the formation of benzoic acid. This may be readily detected by shaking up the oil with a little water, separating the water and saturating it with dry carbonate of potash. The alcohol then rises to the surface and may be recognised by its familiar characters and measured.

Nitrobenzene was introduced about thirty years ago as a substitute for essence of almonds, and, under the name 'Essence of Mirbane,' has been extensively used for scenting soap &c. It is readily distinguished from benzaldehyde by boiling a few drops with ordinary strong nitric acid which is almost without action upon nitrobenzene but converts benzaldehyde into crystalline benzoic acid.

Amber. *Oleum succini.* A mixture of terpenes $C_{10}H_{16}$, boiling at 130° to 400°, obtained by destructive distillation of amber. Mixed with rectified spirit and ammonia formerly used in medicine under the name 'Eau de Luce.' The action of nitric acid upon oil of amber produces a mixture of resinous substances formerly known as artificial musk.

Anise. *Oleum anisi*, B. P. From the fruit of the Star Anise (*Illicium Anisatum*) to the amount of 4–5 per cent. and from the Anise or Aniseed (*Pimpinella Anisum*) under 2 per cent. Consists of a mixture in variable proportions of a dextrorotatory terpene, $C_{10}H_{16}$, and a crystalline solid anisol or anethol

$$C_{10}H_{12}O = C_6H_4(CH_3O)(CH{:}CH.CH_3)[1{:}4]$$

or methyl parapropenyl-phenylate, [21°] (232°) density ·989 at 28°. It constitutes so large a proportion of the oil that this substance is usually semisolid. According to the B. P. the ordinary oil of anise congeals between 50° and 60°F. (10° to 15·5°C.) and may remain solid at 62° or 63°F.; oil of star anise only becomes solid at a few degrees above the freezing-point of water. The statement in reference to the star anise appears, however, to be a mistake, and a more satisfactory test consists in mixing the oil with an alcoholic solution of hydrochloric acid, which gives with the pimpinella oil a pink colour, with the illicium oil a pale brown (C. Umney, Ph., Feb. 1889).

Used as a drug chiefly in cattle medicines, also in making spirituous cordials.

Bergamot. *Oleum Bergamiæ* or *Ol. Bergamottæ.* Prepared in Calabria from the unripe fruit of *Citrus Bergamiæ* by a process similar to that of the *écuelle.* A hundred fruits yield about 2½ to 3 ounces. A small quantity of inferior oil is got by distillation from the residues. This oil contains about a fourth of its bulk of a terpene (Citrene) $C_{10}H_{16}$ (175°–177°), together with compounds of higher boiling-point, which have not been sufficiently examined, but which probably consist of an alcoholic substance $C_{10}H_{17}HO$, and some of its compound ethers. The oil is usually green in colour, owing to the presence of a small quantity of chlorophyll, and it usually deposits a substance called Bergamot *camphor*, but which has no relation to true camphor. Its composition is not known.

Citrene from bergamot is chemically identical with the hydrocarbon from oils of sweet orange and caraway, differing only in the amount of its (dextro-) rotatory power (Tilden and Shenstone, C. J. 1877).

Bergamot is much used in perfumery.

Cajuput. *Oleum Cajuputi*, B. P. Distilled from the leaves of *Melaleuca minor.* A green limpid liquid of peculiar camphoraceous taste and odour, of which the greater part distils between 170° and 180°. Its chief constituent is cajeputol $C_{10}H_{18}O$ (176°–177°), which is identical with cineol from wormseed, and also occurs in the oils of eucalyptus, rosemary, &c. (Wallach, A. 225, 317).

According to Histed (Ph. [3] 2, 804), copper is usually present in the oil, and the green colour naturally due to traces of chlorophyll is thus rendered permanent.

Camphene *v. Terebene.*

Camphine. A name sometimes given to rectified oil of turpentine.

Camphor. A product together with solid camphor from the wood of *Cinnamomum Camphora* and of *Dryobanalops aromatica* imported from Formosa and Japan. An account of its production in Japan has been given by H. Oishi (S. C. I. 3, 353).

Camphor oil is a solution in various proportions of common camphor in a mixture of liquid hydrocarbons and camphoragenol $C_{10}H_{18}O_2$, a heavy oil (212°–213°) (Yoshida, C. J. 1885, 1, 779). The hydrocarbon contains lævogyrate turpentine and dipentine (Wallach). Imported into Europe in much larger quantities than formerly.

Caraway. *Oleum Carui*, B. P. Oil distilled from the fruit of *Carum Carui.* Yield about 4 p.c. A mixture of a terpene $C_{10}H_{16}$ (170°), chemically identical with the terpene of orange and bergamot (though of much smaller rotatory power) with carvol $C_{10}H_{14}O$ (280°). The terpene constitute about one-fifth of the bulk of the oil.

Cascarilla. From the bark of *Croton Eleuteria.* A mixture of a terpene $C_{10}H_{16}$ (172°) and bodies of higher b.p.

Cassia. The oil distilled in China from the bark of an undetermined species of *Cinnamomum.* Consists essentially of cinnamic aldehyde, and closely resembles oil of cinnamon, though of inferior aroma.

Cedar. By distillation from the wood of the red cedar, *Juniperus Virginiana.* A mixture of cedrene $C_{15}H_{24}$ (264°–268°) with cedar camphor $C_{15}H_{26}O$ (282°).

Chamomile. *Oleum Anthemidis*, B. P. From the entire plant of *Anthemis nobilis.* Consists chiefly of isobutyl and amyl angelates and amyl tiglate, with small quantities of isobutyl isobutyrate, and other compounds. By saponification with caustic potash it yields about half its weight of angelic acid $CH_2{:}C(CH_3)CH_2.COOH$ [44°–45°]. Tiglic acid [64·5°] is isomeric with angelic acid. Freshly distilled chamomile oil is usually pale blue, but becomes yellow on exposure to light. The blue substance, also present in oil of matricaria, is, according to Piesse (C. J.), a blue liquid (302°), giving a blue vapour, and containing C 81·21, H 10·95, O 7·84 p.c. According to Kachler (B. 4, 36) the blue oil is almost odourless, boils between 270° and 300°, and has the composition $(C_{10}H_{16}O)_3$.

Cherry laurel. From leaves of *Prunus Laurocerasus* by distillation with water. The oil, seldom prepared except as a by-product in the distillation of cherry laurel water (B. P.), closely resembles oil of bitter almonds. It consists chiefly of benzoic aldehyde with its cyanhydrin and free hydrocyanic acid, together with a small quantity of benzyl alcohol $C_6H_5.CH_2OH$ (Tilden, Ph. [3] 5, 761).

Cinnamon. *Oleum Cinnamomi*, B. P. From the inner bark of *Cinnamomum Zeylanicum* or Ceylon cinnamon. Yield of oil by distillation ·5 to 1 p.c. Density about 1·035, and therefore sinks in water. Yellow when fresh, but deepens in colour by exposure to air. Consists of cinnamic aldehyde $C_6H_5.CH{:}CH.CHO$, with a small quantity of a lævogyrate hydrocarbon, and traces of cinnamic acid. The last is a product of oxidation, and increases upon exposure to air, so as sometimes to crystallise.

The oil distilled from cinnamon leaf contains no cinnamaldehyde, but a mixture of eugenol (*see Cloves*) and hydrocarbons (Stenhouse).

Citron or Cédrat, from rind of the fruit of the citron (*Citrus medica*) by the sponge process, is similar in composition to essence of lemon. According to Hanbury, that which bears its name is for the most part fictitious.

Citronella. Obtained in Ceylon and Singapore from leaves of *Andropogon Nardus*. Consists chiefly of citronellol $C_{10}H_{18}O$ (about 210°). Isomeric with borneol, but requiring further investigation (*see* Wright, C. J. 1874, 317).

Cloves. *Oleum Caryophylli*, B. P. By distillation from the flower-buds of *Caryophyllus aromaticus*. The oil is a mixture of sesquiterpene $C_{15}H_{24}$ (251°) and eugenol $C_{10}H_{12}O_2$ (247–248°). The latter may be separated from the hydrocarbon by shaking up the oil with potash, separating the alkaline liquid, and acidifying. Oil of cloves sinks in water.

Copaiva. *Oleum Copaibæ*, B. P. Copaiva is an oleoresinous exudation from the stem of various species of *Copaifera*, growing chiefly in South America. The volatile oil $C_{20}H_{32}$ (250°–260°) may be separated from the resins by distillation. The resin consists chiefly of copaivic acid $C_{20}H_{32}O_2$ [116°–117°].

Coriander. *Oleum Coriandri*, B. P. From the ripe fruit of *Coriandrum sativum*. Consists chiefly of a compound $C_{10}H_{18}O$, which has not been fully investigated, but which is probably closely allied or identical with cyneol (*see* Wormseed).

Cubebs. *Oleum Cubebæ*, B. P. From the fruit of *Piper cubeba* to the extent of 6 to 15 p.c. (Hanbury). The oil (220°–280°) appears to be a mixture of a sesquiterpene (cubebene) $C_{15}H_{24}$, and a stearoptene $C_{15}H_{26}O$, which sometimes crystallises from old samples.

Cummin. From fruit of *Cuminum Cyminum*. Consists of a mixture of paracymene $C_{10}H_{14}$ (175°) with cuminol or cuminic aldehyde. $C_3H_7.C_6H_4.CHO$ (236·5°), together with small quantities of cuminic acid.

Dill. *Oleum Anethi*, B.P. From the fruit of *Anethum graveolens* by distillation. Similar in composition to oil of caraway.

Eucalyptus. *Oleum Eucalypti*, B. P., obtained by distillation from the leaves of the Australian trees *E. globulus*, *E. amygdalina*, and *E. citriodora*.

These oils are used for scenting soap, and generally in perfumery, and in medicine. The oil of *E. globulus* is pale yellow, and slightly dextrorotatory, and is soluble in about an equal volume of alcohol. It contains a pinene $C_{10}H_{16}$, and another terpene, b.p. 174°, together with some cymene; but the chief constituent (two-thirds) is a liquid formerly called eucalyptol, but now known to be identical with cineol, $C_{10}H_{18}O$ (*v. Santonica*).

Fir wool (*v. Pinus sylvestris*).

Fennel. From the fruit of *Fœniculum vulgare* (*Anethum Fœniculum*, L.). The oil contains the same ingredients as oil of anise (*q. v.*). The French oil of sweet fennel is the most esteemed. The German oil is obtained chiefly from the fruit grown in Saxony.

Geranium. Obtained in France and Germany by distillation from leaves of *Pelargonium radula*. The Indian oil is procured from a grass, *Andropogon Schœnanthus*. The chief constituent of these oils is a liquid isomeride of borneol, $C_{10}H_{18}O$ (232°–233°), possessing an odour like that of rose-oil, and manufactured expressly for adulterating the costly attar. A number of derivatives of geraniol have been obtained (Gintl, J. 1879, 941).

Grass oils (*v. Citronella, Geranium, Verbena*).

Juniper. *Oleum Juniperi*, B. P., from the fruits of *Juniperus communis*. It contains about one-third of its bulk of a slightly lævogyrate hydrocarbon, which is chemically identical with the hydrocarbon from French turpentine (Tilden and Shenstone, C. J., May 1877), together with a mixture of polymeric hydrocarbons, which boil at 180° and upwards.

Lavender. *Oleum Lavandulæ*, B. P., by distillation from the flowers (best without the stalks) of *Lavandula vera*. The English oil commands a high price, and is very superior in perfume to the foreign oil, which is obtained chiefly from the south of France.

Statements regarding the composition of oil of lavender are very conflicting. According to Bruylants (J. Ph. 1879), pure oil of French lavender flowers contains 25 p.c. of a terpene similar to turpentine oil, the remainder consisting chiefly of a mixture of camphor and borneol. The latter substances, however, were not separated in the solid state. Shenstone states (Ph., Sept. 1882) that the English oil yields less than 1 p.c. of terpene. After distillation *in vacuo* the syrupy residue gave no crystalline matter when cooled to a low temperature.

Freshly distilled oil of lavender does not possess its proper fragrance, which is only developed fully after exposure to air in a partly closed bottle.

The oil of lavender used in porcelain painting is the produce of *L. Spica* growing in the south of France. It is commonly called Oil of Spike.

Lemon. *Oleum Limonis*, B.P. Made at Reggio (Calabria) and at Mentone and Nice from the rind of the scarcely ripe fruit of the *Citrus limonum*, either by the sponge or *écuelle* process, by expression, or, of inferior quality, by distillation, from residues. Four hundred fruits yield from 9 to 14 ounces of essence. This oil consists chiefly (about 70 p.c.) of a terpene $C_{10}H_{16}$ (limonene), which boils at 176°, and agrees in several particulars with the citrene from bergamot orange and caraway oils, but differs from that compound in producing a crystalline hydrate or glycol, $C_{10}H_{18}(HO)_2H_2O$, when treated with nitric acid and alcohol, and in its behaviour with nitrosyl chloride and with sulphuric acid. There is also present in lemon oil a small quantity of lævogyrate turpentine $C_{10}H_{16}$ (156°), together with an alcoholic body, $C_{10}H_{17}HO$, and its acetate $C_{10}H_{17}(C_2H_3O)O$, both of which boil at temperatures above 200°. A small quantity of cymene is also probably present (Tilden, Ph. [3] 9, 654, and Conf. 1877). Lemon oil is chiefly used in confectionery and as a perfume.

Lemon oil has been said to change spontaneously into turpentine by keeping. There is, however, no satisfactory evidence in favour of so improbable a hypothesis; the fact being that on exposure to air oxygen is absorbed and a resinous substance of terebinthinate odour formed. The presence of turpentine could easily be recognised by determining the rotatory power of the sample by the polariscope, then heating for a short time to 300°, and again observing the rotation (Berthelot). Turpentine is quickly changed by heat into optically inactive liquids, whilst lemon oil is very slowly affected. The presence of cymene, $C_{10}H_{14}$, of terpilene (dipentene), terpinolene, or terpinene, $C_{10}H_{16}$, all of which smell like lemons, would at once be detected by their want of rotatory power on the polarised ray.

The rotatory power of several genuine samples of essence of lemon examined by Hanbury gave +20·9°, +33·4°, and +28·3° respectively. In a column 50 mm. long, Gladstone found +67·7°, Tilden +61·5° for 100 mm.

Lime. From the rind of the fruit of *Citrus Limetta*, manufactured in Sicily and in Montserrat (West Indies) by the *écuelle* process. This consists chiefly of limonene $C_{10}H_{16}$. The oil distilled from the leaves of the same tree contains the same hydrocarbon mixed with methylnonyl ketone, and terpineol with polymerides, boiling above 280° (F. Watts, C. J. 1886, Trans. 316).

Mace (*v. Nutmeg*).

Mustard. *Oleum Sinapis*, B.P. The oil distilled from ripe seeds of *Brassica nigra* (*Sinapis nigra*, L.) after expression of the fixed oil. Pale yellow; density 1·015 to 1·020 (147°–148°). Miscible with alcohol and ether, and slightly with water. Extremely pungent, and applied to the skin produces a blister almost instantly. Mustard oil is not present in the dry seed, but is produced on the addition of water by the action of a soluble ferment (myrosin) upon a crystallisable glucoside (myronate of potassium, sometimes called sinnigrin); the latter is present in black, but not in white, mustard-seed, which contains a different principle, sinalbin, from which a blistering oil is produced which has a sharp taste but no smell.

$$\underset{\text{Potas. myronate}}{KC_{10}H_{18}NS_2O_{10}} = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Mustard oil}}{C_3H_5CNS} + KHSO_4$$

The quantity of myrosin present in black mustard-seed is sometimes insufficient to develop the maximum quantity of oil; a portion of white mustard may then be added.

Essential oil of mustard is isomeric, not identical, with allyl thio-cyanate $N{:}C.S.C_3H_5$, although it may be formed by heating allyl iodide with a thiocyanate. It presents the characters of an allyl thiocarbimide $S{:}C{:}N.C_3H_5$. When heated for some time it deposits sulphur and yields allylcyanide or crotonitril $C_3H_5.CN$ (118°), which is said to be often present in commercial oil of mustard.

Nutmeg. *Oleum myristicæ*, B. P. Distilled (2–3 p.c.) from the nutmeg, the nucleus of the seed of *Myristica fragrans*. The oil is dextrorotatory, and consists chiefly of a dextrorotatory pinene (156°–160°), formerly called myristicene, together with some cymene and myristicol, $C_{10}H_{16}O$ (212°–218°).

Volatile oil of *mace* has a similar composition.

Orange. *Orange peel.* Two varieties are distinguished in commerce, viz. *Essence de Bigarade* from the bitter orange, and *Essence de Portugal* from the rind of the sweet orange. They are extracted like essence of lemon by the sponge or *écuelle* process, or sometimes by distillation. Portugal has been most carefully studied. The distilled oil consists almost wholly (97–98 p.c.) of a citrene $C_{10}H_{16}$ (175°–176°), which is identical with the hydrocarbon obtained from bergamot, caraway, and some other oils. It is readily distinguished by treatment with hydrochloric acid gas, which forms no monochloride with it, but converts it completely into a dihydrochloride $C_{10}H_{16}2HCl$ [49°–50°] identical with the compound obtained by treating turpentine with hydrochloric acid in the presence of alcohol or water. The pure hydrocarbon has only a faint odour of orange (Wright, C. J. 1873, 552; Tilden a. Shenstone, C. J. 1877; Wallach, A. 227, 289).

Orange leaves. Oil of *petit grain* was formerly obtained from small unripe oranges, but is now made from the leaves and young shoots of either sweet or bitter orange by distillation. According to Gladstone (C. J. 1864), it contains a hydrocarbon probably identical with that from Neroli (*v.* below).

Orange flowers or Neroli. By distillation, carried on chiefly in the flower districts of the south of France. A pure sample examined by Hanbury and Flückiger (Pharmacographia) was characterised by the violet fluorescence of its solution in alcohol. The oil distils chiefly between 185° and 195°, and the residue yields a very small quantity of a crystalline inodorous substance [55°], improperly called camphor. According to Gladstone (C. J. 1863, 549), neroli contains a terpene [173°]. Neroli is usually adulterated with *petit grain*.

Origanum *v. Thyme.*

Peach kernels *v. Bitter almonds.*

Pepper. The oil distilled from black pepper has not been fully examined. It appears to consist chiefly of a pinene $C_{10}H_{16}$ (160°), which, according to Hanbury and Flückiger (Pharmacographia), is lævorotatory.

Peppermint. B. P. The essential oil is obtained by distillation of the flowering herb (*Mentha piperita*), which is cultivated in several places in England, on the Continent of Europe, and in America. The oil consists of a solution in very varying proportions, of menthol or menthyl alcohol, $C_{10}H_{19}OH$, in a terpene or mixture of terpenes. Menthol crystallises in distinct prisms [42°] (212°); it has a powerful characteristic odour, and rotates a polarised ray to the left. Boiled with sulphuric acid, diluted with half its volume of water, menthol acquires a blue colour. Solid menthol is used externally for allaying pain in neuralgia. It is chiefly obtained from Chinese and Japanese oil, which is distilled from *Mentha arvensis*, vars. *piperascens* and *glabra.*

Pimento. *Allspice or Jamaica pepper. Oleum pimentæ,* B. P. The oil distilled in Britain from fruits of *Pimenta officinalis*, Lindl. (*Eugenia pimenta*, D. C.), which yield about 3 to 4 p.c. The oil sinks in water, and closely resembles oil of cloves in composition, consisting of a mixture of a hydrocarbon, $C_{15}H_{24}$, with eugenic acid or eugenol, $C_{10}H_{12}O_2$.

Pinus sylvestris. *Oleum Pini sylvestris,* B. P. The oil distilled from the fresh leaves of *Pinus sylvestris* (Scotch fir) is chiefly imported from Germany under the name of fir wool oil. This liquid is nearly colourless, with an aromatic lavender-like odour, and is soluble in about seven times its volume of rectified spirit. It consists of a mixture of pinene, $C_{10}H_{16}$ (156°), differing from common turpentine in having a stronger dextrorotation (171°), with a lævorotatory hydrocarbon, which forms about two-thirds the bulk of the oil (Tilden, C. J., February 1878). The latter is stated by Wallach (A. 227, 287) to consist of limonene. Limonene from lemons is, however, dextrorotatory.

Rose, Attar or **Otto of.** Obtained by distillation from the flowers of *Rosa Damascena*, cultivated in Turkey, and from other species grown in south of France, in India, and in Morocco. The oil is a pale liquid of density about ·88, which deposits even at common atmospheric temperatures a considerable but variable quantity of a crystalline stearoptene. This when purified is inodorous, melts at 32·5°, and probably consists of a paraffin C_nH_{2n+2} (Hanbury and Flückiger, Pharmacographia). The elæoptene, to which the odour of the 'attar' is due, consists of a compound or mixture of compounds containing oxygen. Nothing is known of its constitution. Commercial attar of rose is very commonly, perhaps always, adulterated with 'geranium' oil, the product of an Indian grass, *Andropogon Schœnanthus.* The addition of this oil diminishes its disposition to crystallise. The stearoptene, however, can easily be imitated by an addition of paraffin, wax, or spermaceti, and there is no good test for the presence of geranium oil.

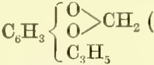
Rosemary. *Oleum Rosmarini.* B. P. The oil distilled from the flowering tops of *Rosmarinus officinalis* growing wild in the south of France. It contains a lævorotatory pinene $C_{10}H_{16}$, ordinary camphor $C_{10}H_{16}O$, borneol, $C_{10}H_{18}O$, and cineol, $C_{10}H_{18}O$ (E. Weber, A. 238, 89). Oil of rosemary turns the plane of polarisation to the right, probably owing to the presence of camphor.

Rue. *Oleum Rutæ,* B. P. Distilled from the fresh herb of *Ruta graveolens.* Consists essentially of methylnonyl ketone $CH_3.CO.C_9H_{19}$ (224°), together with a small quantity of the ketone $C_{12}H_{21}O$. It is doubtful whether the small quantity of terpene found in commercial oil of rue is a natural or an added ingredient.

Sage. From the common sage, *Salvia officinalis.* This consists of a mixture of a terpene identical with the lævopinene $C_{10}H_{16}$ from French turpentine (Tilden and Shenstone, C. J., *loc. cit.*) with ordinary camphor and salviol, $C_{10}H_{16}O$, a liquid (197°–203°) (Muir and Sugiura, C. J. 1878, 1, 292).

Santonica *v. Semina contra.*

Sassafras. By distillation from the root of *Sassafras officinale*, a tree growing in North America. The oil consists chiefly of safrol $C_{10}H_{10}O_2$ [8°] (228°–235°), together with about 10 p.c. of a pinene $C_{10}H_{16}$ (156°) and traces of a phenol. Safrol crystallises in four- or six-sided prisms with the smell of sassafras. It is insoluble in alkalis and optically inactive. By oxidation with potassium permanganate it yields formic, propionic, and piperonylic acids, and is regarded as a derivative of allyl-benzene, thus



$$C_6H_3\begin{cases} O \\ O \end{cases}\!\!>CH_2 \quad C_3H_5$$

$C_6H_3\left\{\begin{array}{l} \left.\begin{array}{l}O\\O\end{array}\right>CH_2 \\ C_3H_5\end{array}\right.$ (Poleck, B. 19, 1094*a*).

Savine. *Oleum Sabinæ*, B. P. Distilled from the fresh tops of *Juniperus Sabina.* The tops yield 2–3 p.c., the berries a much larger proportion of volatile oil. The oil has a pale-yellowish colour, is dextrorotatory, and is usually represented as having the same composition as turpentine oil. The odour is, however, different, and upon fractional distillation only a small quantity of a hydrocarbon comes over at about the b.p. of the pinenes. From this the characteristic nitrosochloride could not be obtained (Tilden and Shenstone, C. J., May 1877). The greater part of the oil consists of a sesquiterpene, $C_{15}H_{24}$ (Wallach, A. 238, 78–89).

Semina contra. *Santonica, Wormseed.* Obtained (about 1 p.c.) from the unopened flowerheads of *Artemisia maritima*, var. *Stechmanniana.* This oil consists chiefly of cineol (176°–177°) $C_{10}H_{18}O$, a liquid of unpleasant camphoraceous odour, and optically inactive (Wallach and Brass, A. 225, 291). It also contains a small quantity of a lævorotatory hydrocarbon. Cineol is probably rather widely distributed, having been already recognised in oils of cajuput, eucalyptus, rosemary, &c.

Spearmint. *Oleum Menthæ viridis,* B. P. The oil is distilled from the fresh flowering herb grown in Britain, in America, or in Germany. It is said to consist of a mixture of a pinene (156°) with a compound $C_{10}H_{14}O$ isomeric with carvol (Gladstone, C. J. 1864, 2, 11).

Terebene is obtained by agitating French or American turpentine oil with successive small quantities of strong sulphuric acid till its action on polarised light is completely destroyed. The acid is then removed by washing with water and a little alkali, and the product distilled in a current of steam. A yellow viscid oil known as 'colophene' remains behind, whilst the distilled liquid, after separation from the water, is clear and colourless. The latter is commercial 'terebene.' It has a peculiar odour resembling that of thyme and camphor, and is used chiefly for inhalation in affections of the throat. It was formerly supposed to contain a specific liquid hydrocarbon (156°), to which the name 'terebene' was given. The products of the action of sulphuric acid upon turpentine have, however, been shown to vary according to the strength of sulphuric acid and the temperature of the mixture. The 'terebene' produced by the action of strong sulphuric acid is now known to consist of a mixture of hydrocarbons, of which inactive camphene, $C_{10}H_{16}$, [51°] (160°) (Armstrong and Tilden, C. J., Nov. 1879) dipentene, $C_{10}H_{16}$, (180°–182°) and isomeric hydrocarbons, terpinene, and terpinolene (Wallach, A. 230, 225), with cymene, $C_{10}H_{14}$, are the chief.

Thyme. *Thymol*, B. P. The red oil of thyme, often called in commerce oil of origanum, is distilled in the south of France. It contains lævogyrate pinene, $O_{10}H_{16}$ (160°), cymene $C_{10}H_{14}$ (175°), and thymol $C_{10}H_{14}O$ (*v. Ajowan*).

Turpentine. *Oleum Terebinthinæ*, B.P. For production, see earlier part of this article.

a. American, from *Pinus australis* and *P. Tæda*. This is the variety which occurs chiefly in English commerce. Oil or spirit of turpentine of good quality should begin to boil about 160° and distil, leaving only a slight residue, below 180°. It consists of dextro-pinene $C_{10}H_{16}$ (156°) with small quantities of oxidation products, resin, and polymeric hydrocarbons.

The specific rotatory power of pure dextro-pinene for yellow light is $[\alpha]_j = +21{\cdot}5°$ (Berthelot).

Commercial turpentine oil varies somewhat in rotatory power, but any great reduction would indicate either the presence of lævogyrate turpentine or of petroleum, which is inactive. The detection of the latter may be effected by treating the oil with sulphuric acid, which polymerises the terpenes present, then distilling in steam and examining the distillate (Armstrong, Turpentine, its Nature and Adulterations, S. C. I., 1, 478). Turpentine oil is miscible with alcohol, ether, and glacial acetic acid, but not with water or aqueous solutions. It dissolves no salts or mineral substances, but readily takes up resins, camphor, and hydrocarbons.

b. French or Bordeaux, from *Pinus maritima*. Similar to American in odour, boiling-point, and solvent powers, but rotates the plane of polarisation to the left; $[\alpha]_j = -42°{\cdot}3$ (Berthelot).

c. Russian and Swedish, from *Pinus sylvestris* and *P. Ledebourii*. These liquids consist of a mixture of two terpenes with oxidation products. The former is identical with the pinene of which American turpentine consists. The latter, called 'sylvestrene,' forms about two-thirds of the whole, and is peculiar to these turpentines (sylvestrene, $D = {\cdot}8612$ at 16°; b.p. 173°–175°; $[\alpha]_D = +19{\cdot}5°$; Atterberg, B. 10, 1203).

These turpentines cannot be used for making varnishes, as they leave a sticky residue which does not dry completely. The chief use of Russian turpentine in this country is in the production of the liquid known as 'Sanitas,' which is employed as an antiseptic and disinfectant. This is a watery solution of an undetermined—probably organic—peroxide made by blowing air through a mixture of the turpentine with water.

Verbena or **Lemon grass.** Obtained from *Andropogon citratus*, a grass cultivated in Ceylon and Singapore. This oil has been very little examined, but probably consists of an oil similar to citronellol.

Wormseed *v. Semina contra.*

Wormwood. Obtained by distillation from the flowering herb of *Artemisia absinthium*. It contains a pinene $C_{10}H_{16}$ (160°), absinthol $C_{10}H_{16}O$ (195°), and a blue oil similar to or identical with the corresponding constituent of oil of matricaria (*v. Chamomile*).

Adulterations.—Some of the more important cases of adulteration have already been referred to.

Of the very voluminous literature on this subject, the following works may be consulted most profitably:—

1. Reports by Schimmel and Company (Ph. [3] xix. 326, 803, 842. 2. Dragendorff, Studies on Essential Oils (Ph. [3] vi. 541, 581, 641, 681, 721). 3. Davies, R. H., The Iodine-absorption Equivalent of Essential Oils (Ph. [3] 19, 821). 4. Concerning the Use of the Polariscope, consult Landolt, translated by Robb and Veley (Macmillan). This book contains the constants of only a few pure hydrocarbons. For the rotatory powers of the crude oils, consult Hanbury and Flückiger's Pharmacographia (Macmillan).

Detection of alcohol.—This is usually quite easy. The essential oil is thoroughly shaken with about ten times its volume of water in a graduated tube; if the oil is appreciably reduced in volume the presence of a considerable quantity of alcohol may be usually inferred. The watery liquid separated from the oil is then distilled, about one-third being collected. The distillate is then tested by saturating it with pure dry potassium carbonate, when, if much alcohol is present, it will separate and rise to the surface, forming a separate layer, which can be recognised by its inflammability, miscibility with water, and solvent powers. If there is not enough to form a separate layer the addition of a little iodine to the alkaline solution will, after a time, cause the precipitation of iodoform in yellow scales possessing a characteristic odour.

Detection of turpentine.—This is very often a difficult matter, especially in those cases in which a small quantity of a pinene is a natural constituent of the oil. Miscibility of the oil with alcohol is sometimes used as a test, but this is quite untrustworthy. In a few cases the polariscope may be used with advantage, but in general there is no effective method short of submitting the oil to a careful fractional distillation and applying chemical reagents to the portion which comes over at about 160°. The pinenes (dextro- and lævo-) are characterised by the following properties: Density about ·860; boiling point 156° to 159°. With HCl gas in absence of water or alcohol form a monohydrochloride $C_{10}H_{16}HCl$ [125°]. With HCl in presence of water or alcohol form a dihydrochloride $C_{10}H_{16}2HCl$ [50°]. With nitrosyl chloride give a compound $C_{10}H_{16}NOCl$ from which by action of alcoholic potash the compound $C_{10}H_{14}{:}N.OH$ is formed

[129°]. Treated with strong sulphuric or phosphoric acids they are readily converted, with evolution of much heat into viscid polymerides (colophene). W. A. T.

OILS, FIXED, AND FATS. Under the names of *fixed oils*, *fatty oils*, *fats*, and *waxes* are classed a number of analogous bodies occurring naturally in animals and vegetables. When of definite chemical composition, they are also producible by synthetical methods.

The term *fixed* or *fatty oil* is generally used for such members of the group as remain liquid at ordinary temperatures, but beyond the physical character of ready fusibility there is no absolute distinction between the liquid and the solid fixed oils or fats. The liquid fats, however, contain a relatively large proportion of olein or other glycerides of readily fusible fatty acids.

The *waxes* possess certain well-defined physical characters, and exhibit differences in chemical composition which distinguish them pretty sharply from the true solid fats. They are, however, in many respects closely related to the fats.

The following are the general properties characterising the true fats and fixed oils:—

1. When pure, the fixed oils are usually colourless or of a pale-yellow colour. Impure and commercial oils vary in colour from light yellow to red, and even to brown and black. Many vegetable oils have a distinct shade of green from the presence of chlorophyll, and show banded absorption-spectra, which is never the case with oils of animal origin.

2. The smell and taste of the fixed oils are often peculiar, and characteristic of their origin. As these characters become less perceptible the more completely the oil is purified, they are probably due to the presence of certain associated and difficultly removable foreign matters, rather than to the constituents of the true oil.

3. The fixed oils and fats are more or less unctuous to the touch, and if dropped in a liquid condition on paper they leave a permanent grease-spot, unless they are crystalline and hard enough to be rubbed off.

4. The fixed oils and fats are not fluorescent, and, as a rule, have no sensible rotatory action on a ray of polarised light. Castor oil is stated to be optically active, and slight rotation is said to have been observed in rape and sesamé oils.

5. The sp.gr. of the fixed oils is less than that of water, varying between the limits of 0·875 and 0·970; but if certain anomalous oils from marine animals be excluded the lowest density for fixed oils is about 0·912 at a temperature of 15°C. In the fluid state, at the temperature of boiling water, the densities of the true fixed oils and molten fats range from 0·850 to about 0·910. The waxes and allied bodies are, when molten, still lighter, their density ranging from ·808 to ·845.

6. The fusing or melting points of the fixed oils vary within wide limits, and are liable to modification in an obscure manner by certain treatment.

7. The fixed oils and fats are practically insoluble in water, but they dissolve somewhat in absolute alcohol or strong spirit, especially when hot, and are readily soluble in ether, chloroform, carbon disulphide, benzene, petroleum spirit, turpentine, and other volatile oils. The various fixed oils and fats are also readily miscible with each other.

8. The fixed oils and fats are composed of carbon, hydrogen, and oxygen, any nitrogen or sulphur existing in particular specimens being due to the presence of albuminous or other foreign matters. The chemical constitution of the fatty oils is discussed in the sequel.

9. The fixed oils and fats are not inflammable at the ordinary temperature, though they may be burnt by means of a wick. As their name denotes, they are not capable of being distilled without decomposition. When heated alone they darken and evolve acrid offensive vapours; and when further heated to about 315°C. (=600°F.) carbon dioxide is evolved, together with peculiarly irritating vapours of acrolein (C_3H_4O), various volatile organic acids, and gaseous, liquid, and solid hydrocarbons. The temperature at which these decompositions occur has been improperly called the 'boiling-point' of the oil, the phenomenon of apparent ebullition being really due to the escape of the gases formed by the decomposition. When caused to pass slowly through a red-hot tube the fixed oils are almost wholly decomposed into volatile products, consisting of carbonic oxide, hydrocarbons, &c.

10. On distillation with superheated steam, fatty oils suffer a simpler decomposition, termed 'saponification,' with formation of glycerol and fatty acids. This change may also be effected by acting on the oil with sulphuric acid or a strong base.

11. If air be excluded, the fixed oils may be preserved unchanged for a lengthened period, but, on exposure to air, many of them thicken with absorption of oxygen, and are ultimately converted (if exposed in sufficiently thin layers) into a yellowish, transparent skin or varnish. Such oils (*e.g.* linseed, walnut, hempseed, and poppy-seed oil) are called *drying oils.* Under certain conditions, as when cotton-waste, shoddy, or hemp is moistened with oil and exposed to the air, the oxidation of the oil becomes so energetic as to lead to considerable elevation of temperature, and even actual inflammation.

12. The *non-drying oils* behave in a different manner on exposure to air. When absolutely free from foreign matter most of them remain unchanged, but commercial specimens gradually turn *rancid*, that is, they gradually lose their colour (and to a certain extent their fluidity), and acquire an acrid, disagreeable taste, and acid reaction to litmus paper. This alteration is generally attributed to the presence of certain foreign matters, such as the cellular substance of the animal or plant from which the oil was extracted. These bodies are supposed to act as ferments, and set free fatty acids, besides producing small quantities of certain volatile acids (*e.g.* butyric, valeric, caproic) of strong odour. By agitating such rancid oil with hot water, and subsequently treating it with a cold dilute solution of sodium carbonate, the products of decomposition may often be removed and the fat restored to its original state. Max Gräger (Zeitsch. angew. Chem. 1889, 62) considers that rancidity is due to the oxidation of the fatty

acids and glycerin in presence of traces of water. The fatty acids break up into acids poor in carbon but rich in oxygen, belonging partly to the fatty and partly to the oxalic series, of which azaleic acid may be artificially prepared by the oxidation of the fatty acids by nitric acid.

Extraction and purification of fixed oils and fats. For the *extraction* of oils and fats from animal tissues it is often sufficient to allow the substance (*e.g.* cod-liver) to become somewhat putrid, when a quantity of oil drains from it, or is obtainable by slight pressure. A further quantity can be extracted by warming or boiling the tissue with water, as is done with blubber. In the case of lard and tallow it is merely necessary to heat the substance alone, and strain the melted fat away from the membranous matter. In the case of a compact tissue like bone, the whole of the fat cannot be extracted by any means short of treatment with a solvent, such as carbon disulphide or petroleum spirit.

The extraction of the fat or oil from vegetable tissues may be effected by boiling the crushed substance with water, or by subjecting it to powerful pressure, either at the ordinary temperature or between plates heated to a little beyond the fusing-point of the fat. The product obtained in the last manner will usually contain more 'stearin' or solid fat than the 'cold-drawn' oil. In either case a certain quantity of the fat is mechanically retained by the tissues, and hence a larger yield can be obtained by the use of carbon disulphide or petroleum spirit, which on being distilled off leaves the fat behind.

The *proportion of oil* or fat yielded by any particular seed or other source depends on the nature and maturity of the seed and on the process employed for the extraction of the oily matter. According to Vohl, the average percentage of oil extracted by solvents from linseed is 27, from hemp-seed 26, from poppy-seed 49, from walnuts 50, and from almonds 52 p.c. According to Voelcker, the proportion of oil in linseed varies from 31 to 38 p.c. the linseed cake containing from a little under 10 up to nearly 16 p.c,; while the oil in cotton-seed cake varies from 6 p.c. in the undecorticated to 16 p.c. in the decorticated. Cocoa-nibs contain on the average about 50 p.c. of fat. These figures must be received with caution, as it is now usual to express the oil from seeds more completely than was formerly the case.

Determination of oils and fats. In the laboratory, the determination of the oil in solid animal and vegetable matters is effected by treating the finely-divided and previously dried substance with a suitable solvent under such conditions as to ensure complete extraction. Carbon disulphide or petroleum spirit may be employed for the purpose, but ether is more satisfactory for general use. It is not so unhealthy as carbon disulphide, and inflammation, due to breakage of the apparatus or other cause, is not so dangerous as when an accident occurs during the use of petroleum spirit.

The *exhaustion* of seeds, bones, shoddy, oil-cakes, milk-residues, &c., may be effected by simply digesting the substance with the solvent at the ordinary temperature, with frequent agitation, in a closed flask. After some hours, the flask should be opened, placed in hot water, and the solvent thus raised to its boiling-point. The liquid is then filtered into a weighed flask, and the residue washed with the solvent. The solution is subsequently evaporated or distilled by a steam-heat, and the residual oil weighed.

The foregoing method is unsatisfactory, as it requires a considerable quantity of the solvent, of which a notable proportion is likely to be lost. Hence an apparatus which will act automatically, and allow of complete exhaustion of the substance by a limited quantity of the solvent, possesses great advantages.

To recover the oil from its solution in the ether or other liquid employed, the solvent should be distilled off at a steam-heat, and the last traces of it removed by placing the flask on its side and heating it in the water-oven until constant in weight. In some cases the complete removal of the solvent is best effected by blowing a gentle stream of air, previously filtered through cotton wool, through the flask while it is maintained at a temperature of 100°C.

In the case of *liquids* containing oil in the form of emulsion, a separation can often be effected by agitation with ether. The extraction of the fat from milk can be effected in this manner if the liquid be previously made slightly alkaline, but it is better to heat the milk to 100° with an equal measure of hydrochloric acid, and agitate the liquid with ether, after cooling.

Purification of oils. The refining or purification of fixed oils is effected in various ways, according to their origin and the impurities it is desired to remove. The following is an outline of the methods of most general application. They may be modified in detail, or combined in a manner suited to any special case.

Action of light.—Simple exposure of a fixed oil to light for a period varying from a few days to as many months will often effect a remarkable improvement. *Linseed* and *seal oils* afford good examples of the success of this treatment.

Action of heat.—By rapidly heating *palm oil* to about 240°C. and maintaining it at that temperature for ten minutes, it is very effectually bleached, and the same is the case if poppy oil be kept at 90 to 95°C. for four or five hours. The same treatment can be advantageously employed in other cases.

Filtration.—Some oils are greatly improved by treatment with animal or wood charcoal. Kaolin, steatite, plaster of Paris, and other substances may often be employed with advantage to effect a semi-mechanical clarification. After such treatment the oil usually requires filtration through canvas bags, which operation also serves to separate spermaceti, stearin, &c., deposited by cooling the oil.

Washing with water.— A very general method of purification consists in agitating the oil with water. This is often conveniently effected by driving in steam through a false bottom or perforated pipe. This treatment can be combined or alternated with any of the others, and if desired, chemical reagents can be added to the water.

Treatment with acids.—A method of very general applicability, and one which, when carefully conducted, is remarkably efficacious, consists in violently agitating the oil, previously heated to about 40°C., if necessary, with from 1 to 2 p.c. of concentrated sulphuric acid, which attacks and chars the impurities without materially affecting the oil. The acid is then allowed to settle, and the supernatant oil well washed with water; or steam is blown into the mixture for a short time, and the acid water allowed to separate from the oil. For 600 gallons of oil about 10 lbs. of sulphuric acid are usually required, diluted with an equal bulk of water. In some cases hydrochloric acid is substituted for sulphuric. Treatment with acid is very suitable as a means of refining most *seed oils* (*e.g.*, rape and linseed oils), and greatly improves some of the fish oils, but the refined product is apt to contain traces of unremoved mineral acid and an undesirable proportion of free fatty acids. These impurities are of no disadvantage if the oil is to be employed for soap-making, but acquire importance if it is to be used for burning or lubrication. Treatment with sulphuric or hydrochloric acid also serves to remove the lime which exists in *bone-fat.*

Treatment with alkalis.—*Cotton-seed oil*, *olive oil*, *sperm oil*, and some others, are advantageously purified by treatment with a solution of caustic soda, the quantity of which must be regulated according to the proportion of free fatty acids and impurities present in the oil. *Cotton-seed oil* contains a notable proportion of a resinous matter which produces a fine blue colour with the alkali. The oil loses considerably in refining, and the proportion of alkali used should be regulated according to the indications of a preliminary laboratory trial. A specific gravity of 1·06 to 1·10 is a suitable strength for the ley, from 10 to 15 p.c. being usually required. The loss in refining cotton-seed oil by alkali is usually from 4 to 7½ p.c., but occasionally amounts to 12 or 15 p.c. Hence it is desirable, before purchasing crude cotton-seed oil for refining, to ascertain what the loss by refining is likely to be. Cotton-seed oil expressed in England from decorticated seed often contains so large a proportion of free acid that purification with alkali becomes practically impossible. Ammonia, sodium carbonate, magnesium carbonate, or milk of lime may sometimes be used with advantage to remove acids from oils. The use of alkali instead of acid for purification is to be preferred in the case of oils intended for use as lubricants or for cooking. The refined cotton-seed oil now extensively used for cooking, &c., is remarkably free from acid.

Treatment with oxidising agents.—A remarkably effective means of clarifying certain *fish oils* consists in heating the liquid by means of steam to a temperature approaching the boiling-point of water, and then blowing a current of air of a similar temperature through the liquid. The treatment must be cautiously conducted, or the rise of temperature may be so great as to cause a notable change in the density and viscosity of the oil, such as occurs purposely in the manufacture of 'oxidised' or 'blown oil.'

Cotton-seed oil and some fish oils may be advantageously refined by boiling them with a solution of bleaching powder, followed by treatment with dilute sulphuric acid. This plan is employed for completing the refining of cotton-seed oil which has been previously treated with a limited quantity of caustic soda. Although economical, the process causes the oil to acquire an unpleasant taste and smell which cannot be removed.

Another very efficient oxidising agent, especially suitable for the treatment of *palm-oil*, is chromic acid, as produced by the reaction of potassium bichromate with a suitable proportion of sulphuric or hydrochloric acid. The oil is melted, strained if necessary, and then agitated at about 50°C. with about 1 p.c. of potassium bichromate previously dissolved in water. To this is added sufficient acid to react with the salt to form potassium and chromic chlorides or sulphates, a slight excess of acid being rather advantageous than otherwise. Some oils, when treated in this manner, retain chromium compounds with remarkable persistency.

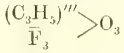
Treatment with reducing agents.—In the case of *linseed* and *other drying oils*, exposure to light in contact with a deoxidising agent affords a very efficient means of clarification. Strips of metallic lead may be employed, or finely divided precipitated lead, as recommended by Livache. A strong solution of ferrous sulphate also answers the purpose, especially if assisted by exposure of the oil to light for some weeks, and accompanied with frequent agitation.

Treatment with precipitants.—*Fish-oils* and some others are greatly improved by violently agitating them with a hot solution of oak-bark or other *tannin-matter*. Steam and air can be blown in at the same time. After deposition, the clear oil should be treated with a solution of acetate of lead or aluminium to remove any excess of tannin, and afterwards dried by treatment with plaster of Paris. Other metallic solutions or reagents forming insoluble compounds with gelatin or albumin may be employed with advantage in certain cases.

Purification by pressure.—This sketch of the principal methods of refining oils would not be complete without a reference to the widely applied use of hydraulic pressure for separating the solid from the liquid constituents of oils. The solid fats thus separated are commercially known as 'stearins,' though they are frequently far from approximating to the pure glyceride of stearic acid. Similarly, the liquid expressed oils are conveniently termed 'oleins,' though of very complex composition. The following are some of the chief instances in which commercial fats and oils are separated by pressure into solid and liquid portions:—

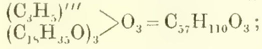
Original oil.	*Liquid product.*	*Solid product.*
Olive oil	Purified olive oil	Olive oil stearin
Cottonseed oil	Purified cotton oil	Cotton oil stearin
Cocoanut oil	Cocoanut olein	Cocoanut stearin
Tallow	Tallow oil	Tallow stearin
Lard	Lard oil	Lard stearin
Whale oil	Purified whale oil	Whale stearin
Sperm oil	Purified sperm oil	Spermaceti

Constitution and chemical properties of fatty oils and waxes. In chemical constitution, all fixed oils and waxes of animal and vegetable origin consist of ethers of the higher fatty acids. The alcohol-radicle with which the fatty acid-radicle is associated to form the natural fixed oils is the triad radicle *glycyl*, C_3H_5. Thus the fixed oils are glycyl esters, or glycerides, and have a constitution expressed by the formula :



$$\left.\begin{matrix}(C_3H_5)'''\\ \bar{F}_3\end{matrix}\right>O_3$$

In this formula $\bar{F}$ represents the radicle of one of the fatty acids, and may have the general formula $C_nH_{2n-1}O$, as the radicle of stearic acid, $C_{18}H_{35}O.OH$; $C_nH_{2n-3}O$, as the radicle of oleic acid ; $C_nH_{2n-5}O$, as the radicle of linoleic acid ; $C_nH_{2n-7}O$, as the radicle of linolenic acid ; or $C_nH_{2n-3}O_2$, as the radicle of ricinoleic acid. Thus, glycyl tristearate, which has the composition :—



$$\left.\begin{matrix}(C_3H_5)'''\\ (C_{18}H_{35}O)_3\end{matrix}\right>O_3 = C_{57}H_{110}O_3\,;$$

is also called tri-stearin, or simply stearin, and is the chief constituent of mutton-fat. Similarly, triolein is the principal component of almond, olive, and lard oils, and tripalmitin of palm oil ; while the glycerides or glycyl ethers of linoleic and linolenic acids constitute the chief parts of linseed and other drying oils. Olein and linolein, being liquid fats, are found most largely in the fluid oils, while stearin and palmitin constitute the major portion of most solid fats.

With a few possible exceptions, that of di-erucin in the solid deposit from rape oil being the best authenticated, the natural glycerides appear to contain three atoms of acid-radicle ; but glycyl monostearate or mono-stearin, glycyl di-stearate or di-stearin, and similar esters, can be obtained artificially by heating glycerol under pressure with the requisite proportion of fatty acid. The constitution of certain of the natural fixed oils is still uncertain, and it is possible that some of them are the esters or ethers of homologues of glycyl, or may have a constitution of a wholly different nature.

While the various vegetable and animal fixed oils and fats consist, as a general rule, of glycerides or glycyl ethers, the *waxes* proper contain the ethers of higher alcohols of the ethylic series. Thus, spermaceti consists chiefly of cetyl palmitate, $C_{16}H_{33}.O.C_{16}H_{31}O$; whilst Chinese-wax, beeswax, and carnaüba-wax contain still higher monatomic alcohols, and the last substance apparently a diatomic alcohol in addition. Sperm oil and bottlenose oil are chiefly composed of bodies having a constitution similar to that of the waxes.

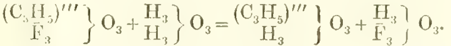
In addition to the glycerides or other esters which constitute the essential portions of the various fatty oils, most natural oils and waxes contain more or less of free fatty acids, and small proportions of colouring, odorous, resinous, and other matters, to which the characteristic colours, smells, and tastes of many of the oils are mostly due. Small proportions of cholesterin and analogous bodies exist in certain oils, and the list of these principles will probably be much extended as accurate examinations of fatty oils become more common than has hitherto been the case.

Free fatty acids in natural oils are usually products of the spontaneous decomposition of the glycerides, a change which is commonly attributed to the presence of mucilaginous or albuminous matters. Over-treatment with sulphuric acid, in the process of refining oils, often results in the formation of free fatty acids, and many commercial oils which have been refined by this process are apt to retain traces of free mineral acid.

The proportion of free fatty acids in oils is best determined by titration in presence of alcohol, with standard alkali and phenolphthaleïn (p. 49).

The *proportion* of free fatty acids present in commercial oils is often very considerable, far larger than is commonly supposed. Thus, in palm oil the free acid, calculated as palmitic acid, usually varies from 12 to nearly 80 p.c. In eighty-nine samples of olive oil intended for lubricating purposes, L. Archbutt (Analyst, 9, 171) found from 2·2 to 25·1 of free (oleic) acid, the mean being 8·05 p.c. In the superior grades of olive oil the proportion of free acid is much smaller. In rape oil the percentage of free acid is generally from 1·5 to 6 p.c. ; but cotton-seed oil, which is refined by means of alkali, is generally free from any trace of free acid (L. Archbutt, S. C. I. 8, 685). The presence of free acid in an oil is doubtless the main, if not the only cause of its tendency to act on metals, and therefore seriously affects the suitability of the oil for use as a lubricant. Burstyn found that the extent of the action of olive oil on brass was regularly and directly proportional to the percentage of the acid present.

Saponification and proximate analysis of fixed oils. When *fatty oils* are heated with water under a pressure of 8 to 12 atmospheres, or are distilled with superheated steam, they react with the elements of water, and are hydrolysed with formation of fatty acids and glycyl alcohol (glycerol, glycerin), according to the equation :



$$\left.\begin{matrix}(C_3H_5)'''\\ \bar{F}_3\end{matrix}\right\}O_3+\left.\begin{matrix}H_3\\ H_3\end{matrix}\right\}O_3=\left.\begin{matrix}(C_3H_5)'''\\ H_3\end{matrix}\right\}O_3+\left.\begin{matrix}H_3\\ \bar{F}_3\end{matrix}\right\}O_3.$$

This method of decomposing fats has met with an enormous application in the industrial production of fatty acids and glycerin.

Many natural oils and fats have a tendency to decompose spontaneously into fatty acids and glycerin, especially in presence of traces of albuminous and other foreign matter. The considerable proportions of free fatty acid often present in commercial palm oil, olive oil, and tallow are due to this cause.

A similar reaction occurs when a fatty oil is heated to 110°C. with about 7 or 8 p.c. of concentrated sulphuric acid. On washing the product with hot water the sulphuric acid and glycerin are removed, and the fatty acids separate in the form of an oily layer.

A parallel reaction takes place when a fatty oil is treated with caustic potash or soda. The change occurs much more readily with some oils than with others, and is greatly promoted by employing heat and using an alcoholic instead of an aqueous solution of the alkali. A potassium or sodium salt, or 'soap' of the fatty acid is produced, glycerol being likewise formed :—

$$C_3H_5'''(O\bar{F})_3 + 3NaOH = C_3H_5'''(OH)_3 + 3NaO\bar{F}.$$

By heating fatty oils with milk of lime, or oxide of lead and water, similar reactions occur, and insoluble soaps are formed, together with glycerol. The method of saponification now most extensively practised on a large scale consists in treating the fat in a closed vessel with 2 or 3 p.c. of lime, and driving in steam at a pressure of 8 or 10 atmospheres. In some works magnesia or oxide of zinc is substituted for the lime.

When a wax is similarly treated with a base it yields a soap of the fatty acid, together with a higher monatomic alcohol, instead of glycerol. The decomposition is usually effected with difficulty, and alcoholic potash or soda should always be the agent employed.

Whenever an ether is split up into a fatty acid and an alcohol the change is called 'saponification,' no matter whether the agent effecting the change be water, an acid, or a base. The term is even extended to the decomposition of ethers or 'esters' which do not yield fatty acids at all.

Quantitative results of saponification.—The saponification of fixed oils by alkalis is a perfectly definite chemical reaction, precisely analogous to the decomposition of the salts of the heavy metals by the same reagents. Thus the saponification of stearin by caustic potash is parallel to the precipitation of bismuth hydroxide from a solution of the nitrate:—

$$(C_3H_5)'''(C_{18}H_{35}O_2)_3 + 3K(OH)$$
$$= (C_3H_5)'''(OH)_3 + 3K(C_{18}H_{35}O_2) ;$$
$$\text{and } Bi'''(NO_3)_3 + 3K(OH) = Bi'''(OH)_3 + 3K(NO_3).$$

Similarly, the saponification of sperm oil resembles the reaction of caustic potash with silver nitrate:—

$$(C_{12}H_{25})(C_{18}H_{33}O_2) + K(OH)$$
$$= (C_{12}H_{25})(OH) + K(C_{18}H_{33}O_2) ; \text{ and}$$
$$Ag(NO_3) + K(OH) = Ag(OH)^* + K(NO_3).$$

The following table shows the composition of the leading proximate constituents of fatty oils, and the theoretical proportions of fatty acid and glycerol resulting from their saponification:—

Glyceride	Chief sources	Formula	Molecular weight	Products of saponification of 100 parts	
				Fatty acid	Glycerol
Glycyl tributyrate (Butyrin)	Butter fat	$C_3H_5(C_4H_7O_2)_3$	302	87·44	30·46
„ trivalerate (Valerin)	Porpoise oil, whale oil	$C_3H_5(C_5H_9O_2)_3$	344	88·96	26·77
„ trilaurate (Laurin)	Cocoanut oil, palmnut oil	$C_3H_5(C_{12}H_{23}O_2)_3$	638	94·04	14·42
„ tripalmitate (Palmitin)	Palm oil, lard	$C_3H_5(C_{16}H_{31}O_2)_3$	806	95·28	11·41
„ tristearate (Stearin)	Tallow, lard, cacao butter	$C_3H_5(C_{18}H_{35}O_2)_3$	890	95·73	10·34
„ trioleate (Olein)	Olive oil, lard oil, almond oil	$C_3H_5(C_{18}H_{33}O_2)_3$	884	95·70	10·40
„ trierucate (Erucin)	Rape oil	$C_3H_5(C_{22}H_{43}O_2)_3$	1052	96·39	8·75
„ trilinoleate (Linolein)	Vegetable drying oils	$C_3H_5(C_{18}H_{31}O_2)_3$	878	95·67	10·48
„ trilinolenate	Linseed oil	$C_3H_5(C_{18}H_{29}O_2)_3$	872	95·64	10·55
„ triricinoleate (Ricinolein)	Castor oil	$C_3H_5(C_{18}H_{33}O_3)_3$	932	95·92	9·88

The following table gives similar information respecting the more important fatty bodies or waxes having the constitution of ethers or 'esters' of monatomic alcohols:—

Ether	Chief source	Formula	Molecular weight	Products of saponification of 100 parts	
				Fatty acid	Monatomic alcohol
Cetyl palmitate	Spermaceti	$C_{16}H_{33}.C_{16}H_{31}O_2$	480	53·33	50·42
Myricyl palmitate	Beeswax	$C_{30}H_{61}.C_{16}H_{31}O_2$	676	37·87	64·79
Ceryl cerotate	Chinese wax	$C_{27}H_{55}.C_{27}H_{53}O_2$	788	52·03	50·25
Dodecatyl oleate	Sperm oil	$C_{12}H_{25}.C_{18}H_{33}O_2$	450	62·67	36·88
Dodecatyl dœglate	Bottle-nose oil	$C_{12}H_{25}.C_{19}H_{35}O_2$	464	63·79	35·78

From an inspection of the first of these tables it will be observed that, with the exceptions of butyrin and valerin, neither of which glycerides ever occurs in a state even of approximate purity in natural fixed oils, all the glycerides which form the chief proximate constituents of natural fatty oils yield approximately equal amounts of fatty acids on saponification, the proportions, if laurin be excepted, being constant within a range of about 1 p.c. Similarly the proportions of glycerin yielded by these same glycerides range within comparatively narrow limits. Hence it may fairly be asserted that the majority of fixed oils yield, on saponification, from 95 to 96 p.c. of fatty acids, and a proportion of glycerol approximating to 10 p.c. Oils containing the glyceride of butyric, valeric, lauric, or erucic acid—such as butter fat, porpoise oil, cocoanut oil, and rape oil respectively—show this peculiarity of constitution in the products of their saponification, and in the case of the first three of these oils the proportion of glycerol resulting from their saponification is correspondingly high.

On the other hand, the bodies formulated in the second table yield, on saponification, much smaller proportions of fatty acids, and, instead of glycerin, give large proportions of higher alcohols of the ethylic series as solid bodies insoluble in water. It is evident that the nature and proportion of the products of saponification sharply distinguish the oils from the sperm and bottle-nose whales from all other fluid fixed oils of commercial interest.

Not only the proportion, but the *nature* of the fatty acids produced on saponification, is of importance in distinguishing the various fixed oils. Thus the drying oils yield chiefly linoleic acid $C_{18}H_{32}O_2$, and linolenic acid $C_{18}H_{30}O_2$, as a liquid product, having a strong affinity for oxygen and combining with a large proportion of bromine or iodine, but not solidified by the action of

* At low temperatures AgOH is said to be formed, this readily splitting up into $Ag_2O + H_2O$.

nitrous acid. The liquid non-drying oils mostly contain oleic acid, which has comparatively little affinity for oxygen, and takes up less bromine or iodine than linoleic acid, but is solidified by treatment with nitrous acid. Rape oil contains erucic acid, which has a very high molecular weight. All the foregoing acids, as likewise their homologues, form lead salts soluble in ether. On the other hand, the higher fatty acids of the stearic series form lead salts insoluble in ether; they are solid at ordinary temperatures, and they do not assimilate bromine or iodine. The lower members of the series (*e.g.*, butyric and valeric acids) are soluble in water, and some of the intermediate members (*e.g.*, lauric acid) volatilise to a notable extent in a current of open steam. Butter fat, porpoise oil, and cocoanut oil are instances of oils containing glycerides of these soluble or volatile fatty acids, and consequently, as already stated, they yield larger proportions of glycerol than the majority of fixed oils.

The proportions of *fatty acids* actually obtained on saponifying the various fixed oils fully bear out the foregoing theoretical views of their constitution, but owing to the difficulty which, till recently, attended its accurate determination, very discordant statements have been made respecting the proportion of *glycerol* actually formed by the saponification of fixed oils, and various ingenious theories have been advanced to account for the supposed deficiency (*v.* Wanklyn and Fox, C. N. 48, 49).

The estimation of the glycerol resulting from the saponification of fatty oils is tedious, and when required is best effected by oxidation to oxalic acid in alkaline solutions by permanganate, the reaction being :—

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O.$$

The process was originally suggested by J. A. Wanklyn and further worked out by W. Fox and Benedikt and Zsigmondy. It has been fully investigated by A. H. Allen and J. C. Belcher, and proved to give very accurate results in the absence of alcohol and other foreign bodies yielding oxalic acid on oxidation. The best way of operating is to saponify 10 grams of the oil at 100°C. with 4 grams of caustic potash dissolved in 25 c.c. of water, in a securely closed bottle which is agitated from time to time. After 10 or 12 hours, or when all oily globules have disappeared, the contents of the bottle are diluted with hot water, when a perfectly clear solution should be obtained. (Except in the case of sperm oil, waxes, and other bodies yielding insoluble higher alcohols on saponification. It is extremely difficult to effect the complete saponification of such bodies by aqueous potash, and methyl alcohol must be resorted to, of such purity that it does not yield oxalic acid by alkaline oxidation with permanganate.) The soap solution is then decomposed by a moderate excess of sulphuric acid, the liberated fatty acids separated, and the aqueous liquid, which must be perfectly clear and free from suspended oily globules, made up to a known measure. One half (= 5 grams of oil) is diluted in a porcelain basin with cold water to 400 c.c., from 10 to 12 grams of caustic potash added, and then a saturated solution of potassium permanganate, till the liquid is no longer green, but blue or blackish. It is then heated gradually and boiled for one hour, when a strong solution of sodium sulphite is added till all violet or green colour is destroyed. The liquid and contained precipitate are poured into a 500 c.c. flask and hot water added to 15 c.c. above the mark, as an allowance for the volume of the precipitate and the increased measure of the hot liquid. The solution is passed through a dry filter, and when cool 400 c.c. (= 4 grams of oil) measured off, acidified with acetic acid and precipitated by calcium chloride. When the precipitate has completely deposited it is filtered off and washed with hot water. It consists chiefly of calcium oxalate, but is liable to contain calcium sulphate, silicate, and other impurities. It may be ignited and the amount of oxalate deduced from the carbonate formed; but a preferable plan is to treat it with dilute sulphuric acid, rinse it off the filter, and titrate the diluted liquid at about 60°C. with a decinormal solution of potassium permanganate (3·162 grams of $KMnO_4$ per litre) each c.c. of which corresponds to ·0045 grams of anhydrous oxalic acid or ·0046 grams of glycerol. The results obtained by this process are satisfactory. Certain acids of the acrylic or oleic series, and possibly oleic acid itself, yield oxalic acid by alkaline oxidation; but the higher numbers of the series (*e.g.* oleic acid) are insoluble in water, and the lower are not known to occur in fixed oils under normal conditions. Butyric acid and other naturally occurring soluble acids do not interfere. The bodies formed by oxidation of linseed oil render the process wholly useless for the determination of glycerol in such products.

In the laboratory (for purposes other than the determination of glycerin) the saponification of oils is best effected by boiling the fatty matter with a solution of caustic potash or soda in strong alcohol. The boiling is continued a short time after the complete disappearance of oily globules. To insure the saponification of the waxes and certain fats, it is desirable to treat the substance with alcoholic potash in a securely closed bottle kept at 100°C. until no more globules are observable. The alcohol is then distilled off or evaporated and the soap dissolved in warm distilled water. A perfectly clear solution will result if a pure fatty oil has been saponified, and the process of saponification has been successfully conducted, but *waxes*, and mixtures containing *hydrocarbon oils* and certain other foreign matters, will give a solution containing oily matter or oily globules in suspension. These admixtures may be removed and determined by agitating the soap solution in a glass-tapped separator with an immiscible solvent, ether being the most generally suitable for the purpose. The ethereal solution is then separated by means of the tap, evaporated at a moderate temperature, and the residue weighed. It is desirable to repeat the above process on the ether residue, to remove any saponifiable matter which may have escaped hydrolysis in the first operation. Treated in this manner sperm and bottlenose whale oils yield about 38 to 40 p.c. of ether residue consisting of solid higher alcohols, and the true waxes behave similarly; but the great majority of fatty oils yield ether residues not exceeding 1 to 1½ p.c. This consists in many cases principally of *cholesterin* (from butter, cod-liver oil, &c.) or *phytostearin* (from vegetable oils). These bodies may be obtained in characteristic crystals by warming the ethereal extract with alcohol, and allowing the filtered solution to cool. *Cholesterin* forms very transparent rhombic plates, the angles of which are extremely well-defined, and constantly measure 79° 30′ and 100° 30′. It melts at 146°. *Phytosterin* or vegetable cholesterin melts at 132°, and forms star-shaped crystals or bundles of long, quite solid, needles. Dissolved in chloroform and treated with strong sulphuric acid, cholesterin gives a cherry-red and phytosterin a blue-red colour. *Isocholesterin,* which occurs together with cholesterin in wool-fat, melts at 137°–138°, and separates from ether in needles, but gives no colour-reaction with sulphuric acid. Its mixture with cholesterin melts at a lower temperature than either substance separately. The following table indicates the behaviour of the constituents of complex mixtures of fats, oils, and waxes, when the aqueous solution of the saponified substance is shaken with ether.

Dissolved by the ether.

- Hydrocarbon oils, including :
  - Shale and petroleum oils
  - Resin-oil hydrocarbons
  - Coal-tar oil
  - Paraffin-wax and ozokerite
  - Vaseline
- Neutral resins
- Unsaponified fat or oil
- Unsaponifiable matter, as cholesterin, phytostearin, &c.
- Higher alcohols, including :
  - Dodecatyl alcohol from sperm and bottlenose oils
  - Cetyl alcohol, from spermaceti
  - Myricyl alcohol, from beeswax
  - Colouring matters, as from palm oil

Remaining in the aqueous liquid.

Fatty acids
Resin acids } in the form of potassium salts
Phenols and phenoloid bodies
Glycerol
Excess of caustic potash

The higher alcohols from sperm and bottlenose oils may be separated from hydrocarbon oils by treating the ether residue with hot rectified spirit, which dissolves the alcohols without notably affecting the hydrocarbons. A more perfect separation of the constituents of a complex ether residue, such as that yielded by a 'recovered grease' or the crude oleic acid obtained by the distillation of such products, is effected by boiling the residue with acetic anhydride (Schulze, J. pr. 115, 163), whereby the alcohols, including cholesterin and isocholesterin, are converted into acetates, which form a lower layer on which the hydrocarbons float. The acetate stratum is separated and boiled with water, to remove the excess of acetic anhydride. The residue is dissolved in hot alcohol, from which the cholesteryl acetate will crystallise on cooling, while the acetates from isocholesterin, sperm oil, and the waxes remain in solution and are precipitated as an oily layer on pouring the liquid into hot water. They may be further examined by ascertaining their melting-points and saponification equivalents, as also the melting-points of the alcohols resulting from their saponification. The acetates of the wax alcohols saponify very readily, and the decomposition of cholesteryl acetate, which is more gradual, is complete when the solution becomes clear. The alcohols will be precipitated on acidulating the solution of the soap, while the fatty acid (acetic) remains in solution, the behaviour being exactly the reverse of that characteristic of saponified fats.

Alcohol radicle	Acetate		Alcohol
	M.p.°C.	Sapon. equivt.	M.p.°C.
Dodecatyl, $C_{12}H_{25}$.	liquid	228	24
Tetradecyl, $C_{14}H_{29}$.	13	252	38
Cetyl, $C_{16}H_{33}$ . .	22–23	284	49·5
Ceryl, $C_{27}H_{55}$ . .	57	438	82
Myricyl, $C_{30}H_{61}$ . .	—	480	85–86
Cholesteryl, $C_{26}H_{43}$.	92	414	144–146
Isocholesteryl, $C_{26}H_{43}$	below 100	414	137–138

The aqueous solution of the soap (containing excess of caustic potash), from which hydrocarbons and higher alcohols have been separated by repeated agitation with ether, may be treated for the contained fatty acids. The liquid should first be well boiled to get rid of dissolved ether. On adding dilute sulphuric acid, preferably in quantity not greater than will suffice to convert the whole of the alkali into $KHSO_4$, a precipitate will be obtained consisting of insoluble fatty acids, resin acids, phenoloid bodies, &c. If the liquid be hot, the precipitate speedily collects as an oily layer at the surface of the liquid. In most cases these fatty acids are almost wholly insoluble in water, and not sensibly volatile at 100°, but by the saponification of butter fat, cocoanut oil, palm-nut oil, porpoise oil, blown oils &c., products are obtained which consist to a notable extent of the lower fatty acids, and hence the mixed fatty acids from these sources are partially soluble in water, and capable of distillation with vapour of water at 100°. For the separation of these soluble or volatile acids from oils containing their glycerides, the layer of fatty acids obtained in the manner above described is boiled several times with water in a flask furnished with a condenser. The distillate and aqueous liquid in the flask will contain volatile and soluble fatty acids, and may be examined either separately or together with the acidulated liquid separated from the layer of insoluble fatty acids. The methods of further examining the nature of the various fatty acids resulting from the saponification are described more in detail on page 48, but the following tabular scheme gives a general method for the proximate chemical analysis of fatty oils and associated bodies. It is liable to variation in detail to suit particular cases, but the same general principle may be adhered to.

From 5 to 10 grammes weight of the sample is a convenient quantity to employ, but if the sp.gr. and other characters of the hydrocarbon oils are required, a larger quantity must be used.

<table>
<tr><td colspan="7">From 5 to 10 grammes weight of the sample (previously melted by warming if necessary) is passed through a dry filter, unless already perfectly clear.</td></tr>
<tr><td rowspan="5">A. Residue may contain <i>curd</i>, <i>salt</i>, <i>water</i>, <i>sand</i>, and <i>insoluble matters</i> generally. It may be washed with ether, dried, and weighed; then ignited gently and weighed again, the loss being the <i>organic matter</i>.</td><td colspan="6">B. The Clear oil. (N.B.—If an aliquot portion of the clarified oil be not blackened when shaken with alcohol and AmHS, and leaves no notable ash on ignition, thus proving the absence of metallic compounds, the following treatments with water and dilute H_2SO_4 may be advantageously omitted, the examination being continued as directed at F*.) The clear oil is agitated in a tapped separator with water and ether. The aqueous solution is separated, and the oil solution again shaken with ether if the previous treatment was found to remove anything.</td></tr>
<tr><td rowspan="4">C. Aqueous liquid contains <i>soaps of the alkali metals</i>. It is evaporated to dryness at 100°, and the residue weighed and further analysed if desired. The <i>alkali</i> may be titrated with H_2SO_4 and methyl orange and the characters of the liberated fatty acids examined.</td><td colspan="5">D. Oil solution. Agitate with dilute H_2SO_4 and separate. Wash residual oil repeatedly by agitation with water till the aqueous liquid no longer reddens litmus.</td></tr>
<tr><td rowspan="3">E. Acid liquid may contain sulphates of <i>Al</i>, <i>Ca</i>, and <i>heavy</i> metals previously existent as soaps. Also <i>boric acid</i> from linseed oil driers, <i>phosphoric acid</i> from bone fat, &c., &c.</td><td colspan="4">F. Solution of oil in ether.* Add a few drops of phenolphthaleïn solution. Then gradually, with repeated shaking, a solution of 2 grammes of NaHO in 10 c.c. methylated spirit 90 of water, in quantity somewhat greater than is sufficient to produce a permanent red colour. Then separate the undissolved oil without delay. Agitate the oil and aqueous liquid respectively with slightly alkaline water and with ether, and add the washings to the main quantities.</td></tr>
<tr><td colspan="2">G. Aqueous liquid. Add methyl orange and then dilute H_2SO_4 till acid reaction obtained. Then as much more dilute H_2SO_4, so as to convert alkali into $KHSO_4$. Agitate or wash separated fatty acids with boiling water.</td><td colspan="2">K. Oil. Evaporate off ether and saponify residual oil by alcoholic potash. Boil off alcohol, dissolve soap in warm water, and agitate cooled solution with ether. Separate and agitate aqueous liquid a second and third time with ether. (In analysis of waxes, treatment of the dry soap with boiling toluene should be substituted for agitation of the solution with ether.)</td></tr>
<tr><td>H. Oily layer, consists of <i>insoluble fatty and resin acids</i>, free in original sample or as soaps of Al or heavy metals. Collect by help of ether, evaporate, weigh, and further examine.</td><td>I. Aqueous liquid. Distil to small bulk, titrating distillate by BaH_2O_2; then evaporate and weigh Ba salts of <i>volatile fatty acids</i>. <i>Non-volatile soluble acids</i> in retort leave Na_2CO_3 when neutralised by NaHO and evaporated or ignited.</td><td>L. Aqueous liquid contains <i>glycerin</i> and <i>soap</i>, formed by separation of neutral fixed oil at sample. Treated as at G, the weight of fatty acids obtained, multiplied by 1·055, gives approximately <i>neutral fixed oil</i> or <i>glycerides</i> of sample. Glycerin may be determined in half of aqueous liquid I, as described on page 21.</td><td>M. Ethereal liquid evaporated at 100° leaves a residue which is weighed, and may contain <i>hydrocarbons</i>, <i>cholesterin</i>, <i>phytosterin</i>, <i>higher alcohols</i>, <i>colouring matters</i>, &c.</td></tr>
</table>

Saponification equivalents of oils. Koettstorfer's process.—The saponification of fatty oils being a perfectly definite reaction, not only can the proportions of fatty acid and glycerol produced from any particular glyceride be calculated, but the proportion of alkali required for the saponification can be similarly ascertained from the general equation

$$C_3H_5(O\bar{F})_3 + 3K(OH) = C_3H_5(OH)_3 + 3K(O\bar{F}).$$

Conversely, if the proportion of alkali required to effect the saponification of a particular oil be accurately determined by experiment, the nature of the glyceride present can be inferred. From the above equation it appears that 1 molecule of a glyceride requires 3 molecules of alkali for its saponification. The number of parts of a glyceride saponified by 1 molecule of alkali will therefore be $\frac{1}{3}$ of the molecular weight; but in the case of the ether of a monatomic alcohol, the number will be identical with the molecular weight. This figure, which really represents the number of grams of an oil saponifiable by one equivalent in grams of any alkali, or, in other words, the number of grams of an oil which would be decomposed by 1 litre of a normal solution of any alkali, is conveniently designated the 'saponification-equivalent' of an oil, and may in all cases be found by dividing the percentage of potassium hydroxide (KHO) required for saponification into 5,610, or the percentage of sodium hydroxide into 4,000. The expression of the neutralising power of oils in saponification-equivalents has the advantage of being applicable to the results of saponification by any alkali, whilst the percentages of caustic potash required for complete saponification are not directly comparable with the figures obtained if soda be the alkali employed. In practice, however, it rarely happens that an oil consists of a single glyceride in a state of even approximate purity, and hence the saponification-equivalents of the natural oils are the resultants of the equivalents of their constituent glycerides, and therefore the quantitative value of the determination is reduced. Nevertheless the peculiarity of constitution of many of the natural oils enables their presence to be inferred from the proportion of alkali required for their saponification.

As hydrocarbon oils do not react with potash, the proportion of these oils in admixture with fatty oils can be deduced from the amount of alkali requisite for the saponification of the sample. Thus, if a sample of so-called 'linseed oil' require only 9·5 p.c. of KHO for its saponification instead of 19·0 p.c. it may be safely assumed to contain 50 p.c. of hydrocarbon oil.

Bromine and iodine absorptions of fixed oils.—Another method of examination based on the chemical constitution of the fixed oils, and which is occasionally of considerable service, is dependent on the percentage of bromine or iodine taken up by the oil under conditions intended to insure the formation of additive compounds only. The fatty acids of the acetic or stearic series are saturated bodies which do not form additive compounds with iodine or bromine, while the acids of the acrylic or oleic series combine with *two* atoms of a halogen, and those of the propionic or linoleic series with *four* atoms of a halogen, and linolenic acid with *six* atoms, as expressed by the following equations. Thus:

Stearic acid, $C_{18}H_{36}O_2$, does not combine with bromine or iodine.

Oleic acid, $C_{18}H_{34}O_2$, forms $C_{18}H_{34}Br_2O_2$, and $C_{18}H_{34}I_2O_2$.

Linoleic acid, $C_{18}H_{32}O_2$, forms $C_{18}H_{32}Br_4O_2$, and $C_{18}H_{32}I_4O_2$.

Linolenic acid, $C_{18}H_{30}O_2$, forms $C_{18}H_{30}Br_6O_2$, and $C_{18}H_{30}I_6O_2$.

The glycerides of the acids of these four series behave similarly to the free acids, so that a determination of the percentage of bromine or iodine assimilated gives a measure of the proportion of olein against palmitin and stearin in a fat, and of the linolein of a drying oil as compared with the olein of a non-drying oil.

Hübl operates on a chloroform alcohol solution of the oil, in presence of mercuric chloride in not less than the ratio $HgCl_2 : I_2$. Under these circumstances chloro-iodo products are formed and the reaction is very definite. The excess of iodine is determined by standard thiosulphate of sodium (*v.*p. 50) (D.P.J. 253, 281; S.C.I. 3, 641).

Oxidation of oils. Drying properties. As already stated, many of the liquid fixed oils thicken on exposure to the air, and, under favourable circumstances, gradually dry up into yellowish transparent varnishes or resins. The oils which possess this property are termed drying oils.

For testing the drying properties of an oil, a definite number of drops of the sample may be placed in a watch glass or flat porcelain capsule, and exposed to a temperature of about 100°C. for twelve or twenty-four hours, side by side with samples of oil of known purity. Olive oil will be scarcely affected by such treatment, and rape oil will only thicken somewhat. Cottonseed oil will form a hard skin or varnish, which can only with difficulty be ruptured by pressure with the finger. In some respects, a preferable plan is to flood a slip of glass with the oil to be tested, in the manner in which a glass plate is covered with collodion. The glass with the adhering film of oil is then kept at 100°, and the progress of the drying watched by touching, at intervals, successive parts of the plate with the finger. Another useful method is to soak a definite measure of thick filter paper in the sample of oil, and then expose it to 100° or 130°C. for some hours, side by side with samples of oil of known purity.

Galletly has pointed out the close relationship which exists between the drying properties of oils and their tendency to inflame spontaneously when exposed to the air in a finely divided condition. He found that when a handful of cotton-waste was imbued with the oil to be tested, and placed somewhat loosely in a paper box in an air bath kept at 80°C., the mass entered into active combustion after a time dependent on the nature of the oil used. Thus, with boiled linseed oil inflammation occurred in little more than an hour, while raw linseed oil required four hours, and rape oil nine or ten, to reach the same stage.

Although frequently grouped as 'drying' and 'non-drying oils, there is no sharp distinction between the two classes. Omitting the oils from marine animals, some of which dry rapidly, the chief commercial liquid fixed oils possess drying properties in the order of the following list, the most rapidly oxidisable being placed first:—Linseed oil, cotton-seed and fancy seed oils, rape oil, earthnut oil, olive oil, animal oleins.

The tendency of the fixed oils to dry or oxidise is in the direct order of their capacity for absorbing bromine or iodine, and of the rise of temperature produced on mixing them with concentrated sulphuric acid.

The chemical changes which occur in the boiling and drying of linseed oil are very imperfectly understood. According to Mulder, part of the linolein is decomposed during the boiling, with the formation of linoleic anhydride, or more probably a more highly oxidised body such as hydroxylinoleic acid. According to W. Fox, the glycerides of the oil are decomposed during the boiling, oxidation products are formed by the fatty acids, and the glycerin splits up into acids of the acrylic series, forming the irritating vapours which always accompany oil-boiling. Acetic and formic acids are prominent constituents of these vapours, and carbon dioxide and water are also eliminated. The statements of Mulder and Fox are probably too sweeping. Allen isolated 8·8 p.c. of nearly pure glycerin from the products of the saponification of linseed oil which had been boiled by the steam process. Bauer and Hazura (M. 9, 459) also consider Mulder's explanation of the drying of linseed oil to be only partially correct. The subject has been recently re-investigated by these chemists, who arrived at the following conclusions:

1. The more linolenic acid an oil contains the more rapidly it dries.
2. The products of oxidation are not merely additive compounds, but contain part of their oxygen as OH groups.
3. The oxidation of the salts of the fatty acids is similar to that of the acids themselves.
4. By very prolonged exposure to air at ordinary temperatures, or by shorter exposure at about 80°C., the fatty acids are fully oxidised, with formation of a resinous sticky solid, insoluble in ether but reconverted into acids soluble in ether on heating with alkali.
5. All the drying properties of oils depend upon the presence of linoleic, linolenic, and isolinolenic acids, as oleic acid forms no solid oxidation product.
6. During the drying of linseed oil only the glycerol of the non-drying glycerides is oxidised, as is shown by the very small quantities of carbonic, formic, and acetic acids formed by passing pure air through pumice soaked in linseed oil. Two samples of linseed oil which were still in the first stage of oxidation, as shown by their being still soluble in ether, contained 8·9 and 12·1 p.c. of free acid. The body insoluble in ether, called by Mulder *linoxyn*, produced by the oxidation of linseed oil, is not an anhydride of hydroxylinoleic acid but a glyceride of that body, which they term *hydroxylinolein.*

The tendency of linseed oil to oxidise is much enhanced by heating it to a high temperature (from 130°C. upwards) while passing a current of air through or over the oil, and subsequently increasing the temperature until the oil begins to effervesce from evolution of products of decomposition. The heating is sometimes effected by direct application of a fire to the bottom of the metallic vessel containing the oil, but a preferable and safer plan is to employ steam. The process is termed 'boiling'; and the oil thus treated is called '*boiled oil.*' By continued 'boiling' the oil becomes very thick and may be drawn out into elastic threads, which are very sticky but do not produce a greasy stain on paper. This product is used in the manufacture of printing ink.

By adding litharge, red-lead, ferric oxide, or manganese dioxide or hydroxide during the process of boiling, the oxidation and consequent drying of the product is still further facilitated. The nature, proportion, and mode of adding these substances is usually kept jealously secret. Lead acetate and manganous borate are among the most approved additions. The action of some of these 'driers' (*e.g.* compounds of manganese) seems to be that of carriers of oxygen, while litharge dissolves in the oil and acts partly as a carrier of oxygen and partly as the base of certain salts which oxidise very rapidly. W. Fox suggests that driers hasten the decomposition of the linoleic acid, with formation of secondary products of acid character which possess the power of combining with metals without evolving hydrogen. It is to those secondary products he attributes the absorption of oxygen.

Blown oils, oxidised oils, base oils.—Various products known by these and similar names are now manufactured by blowing a stream of air through fatty oils. The oils which lend themselves most readily to the treatment are cotton-seed, rape, and linseed oils, but the process is also carried out with olive, lard, and other oils. The oil is usually heated by a steam coil at the commencement of the process to a temperature of 70°C., though this is not strictly necessary, at least with certain oils, and in any case care must be exercised in order to avoid too high a temperature (above 80°C.). The process usually lasts from twelve to forty-eight hours, according to the nature of the oil under treatment, the character of the product desired, and the size and power of the apparatus. Great heat is developed, and the oil gradually increases in density and viscosity. The product can be varied by arresting the process at any particular point. Blown oil is usually of a clear yellow colour, with a disagreeable smell and taste suggesting its origin. It is very viscous and often as dense as or denser than castor oil, from which it differs by not dissolving readily in alcohol and in being soluble in petroleum spirit. Its perfect miscibility with heavy mineral oils gives it an advantage over castor oil in the manufacture of lubricating mixtures for heavy machinery. Mineral oil and castor oil are mutually soluble only to a very limited extent, but by addition of some other oil, such as tallow oil, perfect union can be effected. When the oxidation of cotton-seed oil is pushed to an extreme, the product has a density of ·885 and is not readily miscible with heavy mineral oils. Blown oils yield sebacic acid on dry distillation, and contain but an insignificant proportion of unsaponifiable matter. The odour, taste, and colour reaction of the oil with sulphuric acid will afford an indication of its origin, and more definite information can be obtained by an examination of the physical and chemical characters of the fatty acids produced by its saponification.

The process of blowing results in a change in the fatty acids, a notable proportion of which after the process is soluble in water. The insoluble acids have a mean combining weight considerably below the original, and are regarded by Fox and Baynes (An. 12, 33) as probably 'oxy-acids of the acrylic series.' The glycerin, as determined by the permanganate process, apparently increases somewhat, but this effect is probably due to the formation of soluble products which, like glycerin, yield oxalic acid by oxidation with permanganate. On saponification, blown oils usually yield very dark soaps. The following figures obtained by the analysis of blown oils have been published by Fox and Baynes (*l.c.*):—

—	Linseed	Cottonseed	Rapeseed
Glycerin (apparent)	12·85 p.c.	11·68 p.c.	11·32 p.c.
Free fatty acids	2·73 „	5·35 „	3·70 „
Insoluble fatty acids	87·67 „	85·50 „	84·70 „
Combining weight of insoluble acids . .	258·4 „	196·0 „	186·0 „

W. Fox (Oil and Col. Journ. 1887, 542) has also published the following figures showing the change produced in oils by blowing air:—

—	Linseed		Cottonseed		Rape	
	Before	After	Before	After	Before	After
Specific gravity . .	·9354	·986	·916	·9685	·927	·985
Glycerin . . .	9·36	12·85	9·64	11·32	9·61	11·68
Free fatty acids . .	2·40	2·73	2·50	3·70	3·20	5·35
Insoluble fatty acids .	95·70	87·67	95·43	84·70	95·65	85·50

CLASSIFICATION OF FATTY OILS, &c.

In studying the characters of fixed oils and identifying oils of unknown nature, valuable assistance is obtained from a suitable arrangement of the oils in classes or groups. The classification here adopted is based on a joint consideration of the origin, physical characters, and chemical constitution of the oils. An attempt is likewise made to classify the oils so that each group contains some important commercial oil which is typical of the other members of the group. Thus the oils included respectively in the rape oil, olive oil, and cocoanut oil groups, present a more or less close resemblance to rape oil, olive oil, and cocoanut oil respectively.

The recent researches of Hazura and others have shown that unsuspected differences exist between animal and vegetable oils, and on this account among others it is not found desirable in practice to place in the same group an oil of animal origin (*e.g.* lard oil) with others of vegetable production (*e.g.* almond and olive oils), although in their physical and chemical characters there may be a close similarity. Similarly, the oils from fish and marine mammals are advantageously arranged in a separate class from the oils of terrestrial animals.

It is evident that the melting-point of an oil is chiefly dependent on its chemical composition; oils of which palmitin and stearin are the leading constituents being solid at ordinary temperatures, while in the liquid oils olein or linolein predominates. The specific gravity of the fixed oils is also closely dependent on their chemical constitution, and this becomes more evident when the determination is made at a temperature at which all oils are liquid. Under these circumstances, the waxes are the least dense, then follow the molten fats, the non-drying oils, the drying oils, and lastly castor oil, which is the densest of all natural fatty oils.

I. **Olive oil group.** *Vegetable oleins.* The oils of this group have a density ranging from ·914 to ·920, and hence are lighter than the oils of Groups III., IV., and V. Their viscosity is notably greater than that of the drying oils, but inferior to that of rape oil, and they do not lose their power of producing a greasy stain on paper, however long they may be exposed to the air. They are further characterised by producing very solid elaïdins, and by their moderate saponification-equivalents and iodine-absorptions.

II. **Rape oil group.** The oils of this class are all obtained from the *Cruciferæ.* They are generally classed as non-drying, though less perfect in this respect than the members of Group I., from which they are further distinguished by the greater heat developed when treated with strong sulphuric acid, by their higher iodine-absorptions, by forming pasty elaïdins, and, above all, by their very high saponification-equivalents, a character which is due to the presence of the glycerides of fatty acids of exceptionally high combining weight.

III. **Cotton-seed oil group.** These oils range in specific gravity from ·920 to ·926, or when unrefined somewhat higher. In this character, as also in their elaïdin reactions, iodine-absorptions, and the temperatures developed with strong sulphuric acid, the members of the cotton oil group stand intermediate between the vegetable non-drying oils typified by olive oil (Group I.) and the true drying oils of Group IV.

IV. **Linseed oil group.** *Drying oils.* These oils range in specific gravity from ·924 to ·937, and hence are distinctly denser than the oils of the previous groups, though lighter than those of

Group V. They are not solidified by treatment with nitrous acid, evolve great heat with strong sulphuric acid, and combine with large proportions of bromine and iodine. On exposure to the air in thin layers they absorb oxygen and form varnishes which are at first sticky but afterwards plastic or even brittle. The viscosity of the unoxidised drying oils is less than that of the oils of the preceding groups.

V. **Castor oil group.** The oils of this group have little in common beyond their great viscosity and high density, which ranges from ·937 to ·985. Castor and croton oil are remarkable for their solubility in alcohol and glacial acetic acid, and their marked purgative properties.

VI. **Palm oil group.** The oils of this group are solid vegetable fats not containing notable quantities of glycerides of lower fatty acids. Their melting-points are somewhat variable, and are capable of permanent alteration.

VII. **Cocoanut oil group.** The members of this group are solid vegetable fats, having high densities and low saponification-equivalents. The members of the Sub-group A. contain notable proportions of glycerides of lower fatty acids; that is, of acids distilling with greater or less facility at 100°C. in a current of steam. This character distinguishes them from nearly all other vegetable fatty oils, and from all solid animal oils except butter fat. The members of Sub-group B., though glycerides, are wax-like bodies of peculiar characters.

VIII. **Lard oil group.** *Animal oleins.* This group includes those natural and manufactured oils, fluid at ordinary temperatures, which are obtained from terrestrial animals. They resemble the marine animal oils by darkening under the action of chlorine, but are not turned brown by boiling with caustic alkalis. They do not dry notably on exposure to air, and give more or less solid elaïdins with nitrous acid.

IX. **Tallow group.** *Solid animal fats.* This group comprises such glycerides from terrestrial animals as are solid or semi-solid at ordinary temperatures. Butter fat is distinguished from all other fats of the group by its high specific gravity and lower saponification-equivalent, characters which are due to the presence of a notable proportion of glycerides of butyric and other lower fatty acids.

X. **Whale oil group.** *Marine animal oils.* This group comprises the majority of the fluid oils obtained from fish and marine mammals. They are distinguished as a class by their offensive fishy odour, which becomes more perceptible on warming; by the reddish-brown colour they assume when subjected to the action of chlorine; and by the reddish or reddish-brown colour produced on boiling them with a solution of caustic alkali. With concentrated sulphuric acid they give considerable rise of temperature and colourations varying from light-red to purple and brown. Most members of the group dry more or less on exposure to the air, and yield but little solid elaïdin on treatment with nitrous acid. In these respects they resemble the vegetable oils of the cotton-seed group, and have a similar density. The oils from the sperm and bottlenose whales are peculiar, both as to their physical characters and chemical constitution, and form a separate class (Group XI.). 'Train oil' includes the oil from the blubber of any marine mammal.

XI. **Sperm oil group.** *Liquid waxes.* The members of this group differ from all the fatty oils of previous classes in not being glycerides, but consisting essentially of esters of monatomic alcohols of the ethylic series, in which respect they resemble the true waxes, but are fluid at the ordinary temperature. They are less dense than the glycerides, both at the ordinary temperature and at the boiling-point of water; and on saponification yield considerable proportions of solid higher homologues of ethyl alcohol. They do not dry or thicken notably on exposure to air, but they yield solid elaïdins on treatment with nitrous acid.

XII. **Spermaceti group.** *Waxes proper.* The members of this group are substances solid at ordinary temperatures and more or less resemble beeswax, the prototype of the class. They consist essentially of compound ethers or 'ethereal salts' of the higher alcohol-radicles of the ethylic series, with, in some cases, an admixture of higher monatomic alcohols and higher fatty acids in the free state. Carnaüba wax seems also to contain diatomic alcohol-radicles. Sperm and bottle-nose oils (Table XI.) resemble the waxes in constitution, but are liquid at ordinary temperatures. The bodies known as Japan wax and myrtle wax (Table VII.) are glycerides and not true waxes. Paraffin wax and mineral wax are hydrocarbons, and hence quite different in chemical constitution from the true waxes of animal and vegetable origin.

In the following tables (pages 28 to 34) the chief fatty oils and waxes of commercial or scientific interest are arranged in twelve groups on the principles above described.

IDENTIFICATION OF FIXED OILS.

The recognition of an unmixed animal or vegetable oil may be usually effected by a careful determination of certain of its physical and chemical properties, with such assistance as can be obtained by observations of its colour, taste, smell, &c. Among the physical characters of most service for the identification of an oil, determinations of the melting and solidifying point of the oil and the fatty acids therefrom, of the specific gravity, and of the viscosity, are the most important; though observations of the index of refraction, optical activity, absorption spectrum, and other characters are occasionally useful, as also is the behaviour of the oil with certain solvents. Among the chemical characters of oils, the proportion of alkali necessary for saponification and the amount and nature of the products of the reaction are of the first importance as means of identification. Valuable assistance is also derived from observations of the iodine-absorption, the rise of temperature on treatment with strong sulphuric acid, the nature of the products of oxidation in alkaline solution, the behaviour with nitrous acid, chloride of sulphur, and other reagents. In addition, certain colour-reactions afford valuable indications of the presence of particular oils.

Of the various methods above referred to some of the most important have already been described. The only other methods requiring further notice are the observation of the be-

I. OLIVE OIL GROUP.

Kind of oil	Source of oil	Specific gravity at 15° to 15·5°C. (= 59° to 60°F.)	Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
Olive oil	Fruit of *Olea Europæa.*	·914 to ·917	+ 4 to − 6	285 to 296	81·5 to 84·5	Yellow to olive green; pleasant flavour; easily turns rancid. Contains glycerides of oleic, linoleic, and palmitic acids, with traces of stearic and arachidic. Adulterated with lard oil, earthnut, rape, sesame, cotton-seed, poppy, and mineral oils, and oleic acid.	Lubrication; greasing wool; turkey red dyeing; burning, cooking and eating; soap making.
Olive-kernel oil.	Kernels of the olive (*Olea Europæa*).	·920	—	298	82	Extracted by CS_2 or other solvents. Dark-greenish brown. Said to be very soluble in glacial acetic acid. Oil extracted from pressed olive marc resembles kernel oil, has dark colour and unpleasant smell, and usually gives no solid elaïdin.	—
Almond oil	Nuts of *Amygdalus communis.*	·914 to ·920	− 10 to − 20	287	96 to 99	Yellow and nearly colourless; bland, agreeable taste. Composition similar to olive oil. Adulterated with apricot and peach kernel oils, cotton-seed, poppy, earthnut, lard, and olive oil.	Ointments and emulsions.
Peach oil	Kernels of *Prunus Persica.*	·918 to ·920	Below 20	297	99 to 103	Closely resembles almond oil	Substitute for almond oil.
Apricot oil	Kernels of *P. Armeniaca.*	·918 to ·920	Below 20	291	98 to 102	Closely resembles almond oil	Substitute for almond oil.
Earthnut oil, Arachis oil, Peanut oil.	Nuts of *Arachis hypogæa.*	·916 to ·920	− 5	289	91 to 105	First runnings have density of ·916, the last of ·920. Yellow, or nearly colourless. Pleasant nutty flavour.	Substitute for and adulterant of olive, lard, neats-foot, and other oils. 'Nut-sweet oil' is a mixture of earthnut and olive oils.
Tea oil	Seeds of *Camellia oleifera.*	·917	Very low	287	—	Closely resembles olive and almond oils. Forms firm elaïdin. (*v.* Ph. [3] 15, 634.)	—

II. RAPE OIL GROUP.

Kind of oil	Source of oil	Specific gravity		Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief application
		At 15° to 15·5°C. (=59° to 60°F.)	At 100°C.					
Rape-seed oil, Colza oil.	*Brassica campestris, B. napus,* and allied species.	·914 to ·916	·863	− 6 to − 10	314 to 328	97 to 105·6	When unrefined, yellowish-brown or brownish-green viscid liquid, with peculiar odour and pungent taste. When refined, light yellow, and nearly odourless. Said to be sometimes fluorescent and lævorotatory. Contains glycerides of erucic or brassic and rapic acids, with a little behenia. Sometimes contains sulphur compounds. Gives a very imperfect elaïdin	Used for burning and lubricating machinery. Adulterating olive oil. Soap-making. Greasing steel goods.
Chinese cabbage oil.	Seeds of *Brassica sinensis.*	·914	—	− 12	320	—	Dark, disagreeable odour. Elaïdin like rape oil (*v.* Ph. [3] 634.)	—
Oil of black mustard.	Seeds of *Sinapis nigra.*	·916 to ·920	—	− 18	322	English 95 American 85	Reddish or brownish yellow. Pasty elaïdin. In composition resembles rape oil.	As a substitute for rape oil.
Oil of white mustard.	Seeds of *Sinapis alba.*	·914 to ·916	—	Very low	—	—	Characters similar to oil of black mustard	As a substitute for rape oil.

Kind of oil	Source of oil	Specific gravity At 15° to 15·5°C. (=59° to 60°F.)	Specific gravity At 98° to 100°C.	Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
Cotton-seed oil	*Gossypium barbadense* and allied species.	·922 to ·930	·867 to ·873	1 to 10	285 to 294	105 to 109	When crude, ruby red, or reddish brown, and gives blue colouration when saponified. When refined, straw or golden yellow. Deposits much stearin on cooling. Bland, agreeable taste.	Cooking; manufacturing margarine; compound lard; soap-making; adulterating other oils; in U.S. ointments.
Cress-seed oil	*Lepidium sativum*	·924	—	−15	—	—	Brownish yellow. Taste acrid and disagreeable. Moderately siccative.	—
Grape-seed oil	*Vitis vinifera*	·920	—	−15 to −17	—	—	Light yellow, becoming darker on keeping. Odourless; mild taste; dries slowly.	—
Maize oil	Seed of *Zea Mays*	·917 to ·920	—	—	—	119	Yellow; more viscous than olive or cotton-seed oil. Irritating vapours on heating.	—
Sesamé or teel oil	Seeds of *Sesamum orientale* or *indienne*.	·921 to ·924	·868	+5 to −5	294	103 to 110	Pale yellow; odourless; bland and agreeable taste. Gives magenta colour with sugar and hydrochloric acid.	Cookery; pharmacy; margarine; soap-making, and adulterating almond and olive oils.
Sunflower oil	Seeds of *Helianthus annuus*; *H. perennis*.	·924 to ·926	—	−15	—	132	Yellow. Consists chiefly of linolein with but little olein. (Hazura, M. 10, 190.)	Wool dressing; burning; soap making; adulterating olive oil.
Hazelnut oil	*Coryllus avellana*	·920 to ·926	—	−10 to −19	—	—	Light or amber yellow; viscid; mild, sweet taste; no marked smell; soon becomes rancid.	Perfumery: in pharmacy as a substitute for almond oil.
Camelina oil	Seeds of *Myagrum sativum* (Gold of Pleasure).	·925 to ·926	—	−18 to −19	—	—	Yellowish; peculiar taste and smell; dries slowly	Burning; painting.
Beechnut oil	*Fagus sylvatica*	·920 to ·922	—	−3	—	—	Clear yellow; odourless; tasteless or slightly acrid	In France, for cooking; burning, and soap making.

IV. LINSEED OIL GROUP.

Kind of oil	Source of oil	Specific gravity At 15° to 15·5°C. (=59° to 60°F.)	Specific gravity At 100°C.	Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
Linseed oil	*Linum usitatissimum*; *L. perenne*	·930 to ·939	·881	−20 to −27	288 to 300 (291 to 295 T. and B.)	154 to 160 (T. and B. 173 to 188)	Contains chiefly glycerides of linolenic acid and isolinolenic acid, with some linolein and stearin.	Painting, varnishes, &c.; soft-soap; oilcloth making; adulterating rape oil.
Hempseed oil	*Cannabis sativa*	·925 to ·931	—	−15 to −28	290	143 to 160	Greenish yellow, becoming brown on keeping; disagreeable smell and insipid taste. Often mixed with linseed oil. Sometimes coloured by indigo.	Painting, varnishes; soft-soap making.
Poppy-seed oil	*Papaver somniferum.*	·924 to ·927	—	−18	290	134 to 137	Straw yellow; limpid; odourless; almond flavour (no narcotic properties). Much resembles olive oil. Soluble in 25 parts of cold or 6 of boiling alcohol. Dries rapidly.	Culinary purposes; burning; painting; adulteration of olive oil.
Tobacco-seed oil	*Nicotiana tabacum*	·923	—	−25	—	—	Greenish yellow; inodorous; mild taste; highly siccative.	—
Weldseed oil	*Reseda luteola*	·936	—	Below −15	—	—	Dark green, thin; nauseous odour and taste. Dries rapidly	—
Nigerseed oil	*Guizotia oleifera*	·924 to ·928	·873	Below −9	268 to 295	133	Pale yellow; sweet; more limpid than rape oil. Dries readily and completely at 100°C.	Adulteration of rape oil; substitute for linseed oil.
Walnut oil	*Juglans regia*	·925 to ·927	—	−18 to −28	286	142 to 144	Greenish or yellowish, becoming lighter on keeping; syrupy; agreeable faint smell and nutty taste when fresh, afterwards acrid. Highly siccative.	Paints and varnishes.
Scotch firseed oil	*Pinus sylvestris*	·931	—	−30	—	—	Brownish-yellow. Dries easily.	

V. CASTOR OIL GROUP.

Kind of oil	Source of oil	Specific gravity		Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
		At 15° to 15·5°C. (=59 to 60°F.)	At 100°C.					
Castor oil	Seeds of *Ricinus communis.*	·958 to ·970	·909	−18	309 to 319	84 to 85	Very viscous. Contains glyceride of ricinoleic acid. Not readily soluble in mineral oils. Soluble in 4 measures of cold rectified spirit, or in own measure of cold glacial acetic acid.	In medicine. Making cheap, transparent toilet soaps. Lubricating heavy machinery. Making turkey-red oil.
Croton oil	Seeds of *Croton tiglium.*	·940 to ·942	—	—	—	—	Straw to brownish-yellow. Viscid density increases with age. Contains acrid croto-oleic acid, free, and no glycerine. Taste at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Easily soluble in acetic acid. Produces pustules when applied to the skin. Gives little or no solid claïdin. Thickens somewhat on exposure to air. Contains glycerides of tiglic, crotonic, valeric, and other volatile acids, besides lauric, myristic, palmitic, and stearic. H_2SO_4 turns oil red, chocolate, and black.	In medicine.
Curcas oil	Seeds of *Curcas purgans* or *Jatropha curcas* (purging-nut).	·919 (?)	—	·9 to ·0	204	127	Agreeable almond-like taste. Faintly yellowish colour. Peculiar odour, but not readily soluble in alcohol. Contains glyceride of ricinoleic acid. Insoluble acids 88 per cent.	Substitute for castor-oil. Said to be added to olive oil.
Japanese or Chinese wood oil	Seeds of *Aleurites cordata,* or *Elæococca vernicia.*	·937 to ·940	—	Below −13	266	—	Brown colour and persistent disagreeable odour. Sometimes colourless and odourless. Dries very rapidly, but forms semi-solid product with nitrous acid. Gives very firm black clot with sulphuric acid.	As a drying oil.
Manufactured.								
Boiled linseed oil	Made by heating linseed oil	·939 to ·950	—	—	298	—	Dries rapidly, and often leaves on ignition a residue containing a heavy metal. Adulterated with rosin and rosin oil.	Paints, varnishes, oil-cloth making.
Blown oils	Made by oxidation of rape, cotton, linseed, lard, and other oils.	·942 to ·985	—	—	275 to 284	—	Highly viscous; miscible with mineral oils. Gum on exposure to air. Contain soluble fatty acids. Sometimes adulterated with rosin oil.	Substitutes for castor-oil for lubricating.

VI. PALM OIL GROUP.

Kind of fat	Source of oil	Specific gravity		Melting-point. °C.	Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
		At 15° to 16° C.	At 98° to 99° C.						
Palm oil . .	Fruit of *Avoira elais* or *Elais guineensis.*	·920 to ·927	·857 to ·861	25 to 36	20 to 36	277 to 286	48 to 54	Varies much in consistency, odour and colour. Orange, red, or brown. Often contains much water and free acid.	Railway grease; soap-making when saponified; for candles, &c.
Cocoa butter .	Nuts of *Theobroma cacao*	·995	·857 to ·858	30 to 34	20·5	280	31 to 35	Colourless; chocolate-like taste and smell. Not liable to become rancid.	Pharmacy; chocolate 'creams'; high-class toilet soaps.
Nutmeg butter Mace butter .	Nuts of *Myristica fragrans*	—	·898	45	41 to 42	281	—	Reddish yellow or mottled; taste and odour of nutmeg; firm consistence. Occurs in commerce in oblong cakes covered with leaves. Soluble in four parts of hot alcohol. Contains 6 per cent. volatile oil, free myristic acid and myristin and stearin.	Pharmacy; high-class soaps.

Shea or galam butter.	Seeds of *Bassia Parkii* (Tropical Africa).	—	·859	28	23 to 35	305	—	White, grey greenish or reddish; faint characteristic cacao-like odour and agreeable flavour. Somewhat resembles tallow.	**Soap-making.**
Mahwah butter.	Seeds of *Bassia latifolia* (Tropical Africa)	—	—	45	—	—	—	Greenish or yellowish.	
Bassia or illipe oil.	Seeds of *Bassia longifolia* (India) and allied species	·947	—	33	31	281	—	Greenish; rancid taste; consistency of butter .	Soap-making, when tallow and palm oil are scarce.
Chinese tallow .	Berries of *Stellingia sebifera.*	—	·864	32	30 to 32	—	—	Greenish or white; turns brown on exposure. Faint odour.	—
Manufactured.									
Cotton-seed stearin.	From cotton-seed oil.	—	—	—	—	285 to 294	—	Resembles tallow.	Adulteration of lard; manufacture of margarine.

VII. COCOANUT OIL GROUP.

Kind of fat	Source of fat	Specific gravity		Melting-point °C.	Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
		At 15° to 16°C.	At 98° to 100°C.						
A.									
Cocoanut oil .	Nuts of *Cocos nucifera* and *C. butyracea.*	—	·868 to ·871	20 to 28	16 to 18	209 to 228	7 to 9	Consistency of butter. White or slightly coloured; readily turns rancid. Tastes of cocoanut. Contains glycerides of all acids of acetic series containing even number of carbon atoms, from caproic to arachidic. Chiefly Laurin.	Marine soap; night lights; factitious butter and lard.
Palm nut or palm kernel oil	Kernel of nut of *Avoira elais* or *Elais guineensis.*	·952	·866 to ·873	26 to 30	21 to 26	227 to 255	12 to 15	Resembles cocoanut oil in characters and composition. Usually pink or primrose tint, and peculiar taste and smell.	Substitute for cocoanut oil.
Laurel oil .	Fruit of *Laurus nobilis* (Bay laurel).	—	·878	—	—	270	—	Consistency of butter, green colour, aromatic, and peculiar taste and smell. Melts to a green liquid. Contains glycerides of acetic, lauric, and myristic acids, with stearin, palmitin, olein, &c.	Veterinary and quack medicines.
Macassar oil .	Seeds of *Schleichera trijuga.*	·924	—	28	—	219	53	Buttery. Yields 91 per cent. insoluble acids; glycerides of acetic, butyric, lauric, arachidic, and oleic acids (S. C. I. 8. 722).	—
B.									
Japan wax .	Berries of *Rhus succedanea,* &c.	·984 to 1·000	·874 to ·877	50 to 53	42 to 52	252 to 267	4·2 to 5·6	Greenish or yellowish; tallowy or wax-like.	Candle-making.
Myrtle wax .	Berries of *Myrica cerifera.*	·995	·875	40 to 44	39 to 43	265 to 270	—	Hard; pale green.	Candle-making.

VIII. LARD OIL GROUP.

Kind of oil	Source of oil	Specific gravity at 15° to 16°C.	Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
Neatsfoot oil	The feet of various animals.	·914 to ·916	Below 0	299	66 to 72	Yellowish; odourless; bland taste. Not liable to become rancid. Often adulterated with bone oil, lard oil, and fish oils. Forms pasty elaïdin.	Lubricating clocks and machinery exposed to low temperatures. Leather dressing.
Bone oil	Extracted from bones by boiling or solvents.	·914 to ·916	Variable	—	—	Yellowish to dark brown. Often contains calcium phosphate in notable quantity, which may be detected by the ash left on ignition, and separated by agitating the oil with dilute hydrochloric acid.	Soap-making.
Manufactured.							
Lard oil	Obtained by pressing lard.	·915	−4 to +10	290 to 296	47 to 76	Very slightly coloured; clear; slight odour of lard. Soluble in an equal weight of boiling alcohol. Adulterated with earthnut oil, &c.	Lubricating; soap-making; adulterating olive oil; and wool-greasing; and in America as a lighthouse oil.
Tallow oil	Obtained by pressing tallow.	·916	0 to +6	—	—	Viscid. Much resembles lard oil. Crude oleic acid is often miscalled 'tallow oil.'	

IX. TALLOW GROUP.

Kind of fat	Source of fat	Specific gravity at 98° to 100°C.	Melting-point °C.	Solidifying-point °C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
Tallow; Suet	From the ox and sheep	·856 to ·859	36 to 49	33 to 48	283 to 290	Beef 34 to 46 Mutton 33	Melting-point varies much with part and nature of animal yielding the fat.	Candles; soap-making; lubricating.
Lard	From abdomen and other parts of the hog.	·859 to ·860	28 to 45	27 to 44	286 to 292	55 to 62	Melting-point varies much with part of animal yielding the fat.	Cooking; soap-making.
Horse fat	From the horse, &c.	·861	—	—	—	—	Yellow or dirty white to brown. Consistency of lard, or harder; very variable in quality.	Soap-making. Said to be used for making factitious butter.
Marrow	From beef bones	·858	—	—	285	45	Very variable in character.	Soap making.
Bone fat	Bones of various animals	·859	—	—	284 to 294	47	Brownish; unpleasant smell. Usually softer than lard. Commonly contains lime.	Cheap 'Brown Windsor' soaps.
Wool fat (suint)	The wool of various kinds of sheep.	·888	—	—	330	—	Tough, dirty, yellowish brown. Contains a notable quantity of cholesterin. Takes up much water.	Usually distilled with steam to obtain oleic and stearic acids.
Butter fat	Cow's milk	·867 to ·870	29 to 35	20 to 30	241 to 253	19 to 38	Yellow; pleasant taste and smell. *Butter* contains salt, water, and curd, removable by melting.	Food. Cooking.
Manufactured.								
Margarine	Made from the less solid parts of animal fat (ox, sheep, hog) with admixture of earthnut, sesamé, cotton-seed or cocoanut oil, and salt, milk, &c.	·859 to ·863	34 to 40	18 to 38	285 to 290	50 to 56	Closely resembles butter, of which it often contains a considerable proportion.	Food. Cooking.
Compo-lard.	Hog's fat mixed with beef or mutton stearin, cocoanut oil, cotton-seed oil, &c.	·863 to ·868	—	—	—	63 to 85	Closely resembles lard.	Cooking.
Stearin	Obtained by pressing lard or tallow.	·858 to ·860	54 to 58	—	285 to 293	—	The melting-point is high. Closely resembles hard tallow or suet. Must not be confused with stearic acid.	Candles and night-lights; soap-making.
Recovered fat; Yorkshire grease	Treatment of soapsuds, &c., with acids.	—	—	—	—	—	Grey, brown, or black; very variable; often contains wool-fat.	Cheap candles, soap, &c.

X. WHALE OIL GROUP.

Name of oil	Source of oil	Specific gravity at 15° to 16° C.	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
Whale oil . .	Blubber of *Balæna mysticetus* and various allied species	·920 to ·931	250 to 296	110 (T. and B.)	Yellow or brown colour; disagreeable fishy odour, removable by bleaching powder. Deposits stearin when cooled. Some varieties dry rapidly. Sometimes contains valerin.	Illumination; saw-hardening; soap-making.
Porpoise oil .	Blubber of *Delphinus phocæna* and allied species	·920 to ·930	255 to 256	131	Yellow or brown. Much resembles whale oil. Contains valerin. For the characters of porpoise jaw oil *v.* R. W. Moore, A. C. J. 11, 155.	Illumination; soap-making; leather-dressing, lubrication.
Blackfish oil .	Body of black-fish .	—	284	99	A. C. J. 11, 115	Lubricating fine machinery.
Seal oil . .	Blubber of *Phoca* of various species	·924 to ·929	286 to 301	142 to 152 (T. and B.)	Colour ranges from brown to nearly water-white. Smell disagreeable, but much improved by exposing the oil to air and light. Dries slowly.	Burning in safety lamps; lubrication; adulteration of cod liver oil. Produces a very offensive-smelling soap.
Menhaden oil .	*Alosa menhaden* .	·927 to ·933	292	148 to 160	Brownish colour; fishy odour; dries readily. Sometimes adulterated with mineral oil.	Adulteration of linseed oil.
Cod-liver oil .	Liver of various species of *Gadus*	·925 to ·930	263 to 303	159 to 166 (T. and B.)	Nearly colourless to brown. Disagreeable fishy taste. Contains cholesterin, traces of iodine, certain peculiar principles, and glycerides.	Medicine; leather-dressing.
Shark-liver oil .	*Squalus maximus* (basking shark or sun-fish) and allied species	·911 to ·928	316 to 400	268	Clear yellow colour. Often enormously adulterated. Contains a notable proportion of cholesterin.	Leather-dressing; adulteration of cod-liver oil. (Not now in the market.)

XI. SPERM OIL GROUP.

Kind of oil	Source of oil	Specific gravity		KHO p.c. for saponification	Saponification equivalent	Iodine absorption	Other characters, composition, &c.	Chief applications
		At 15° to 16°C.	At 98° to 100°C.					
Sperm oil . .	Blubber and cranial cavities of *Physeter macrocephalus.*	·875 to ·884	·822 to ·830	12·3 to 14·7	380 to 454	81·3 to 85	Yellow: slightly unpleasant fishy smell. Deposits crystals of spermaceti on cooling. Contains oleate or physetoleate of $C_{12}H_{25}$ and homologues. The alcohol, $C_{12}H_{25}.OH$, and homologues, are obtainable as solid products (36 to 40 p.c.) by agitating solution of saponified oil with ether and evaporating ethereal solution.	Lubrication of light machinery; hardening steel weapons
Doegling oil, or bottlenose oil.	Blubber, &c., of *Hyperoodon rostratus* and *H. bidens.*	·876 to ·881	·823 to ·828	12·3 to 13·4	419 to 456	80 to 82	Closely resembles sperm oil in character and composition. Said to contain dodecatyl dœglate $C_{12}H_{25}, C_{19}H_{35}O_2$.	Substitute for sperm oil, under the name of 'Arctic sperm oil.'
Dolphin oil .	Blubber, &c., of *Delphinus globiceps.*	·922	—	—	—	—	Citron yellow; odour at once fishy and like leather: Soluble somewhat readily in alcohol. Deposits spermaceti when cooled, and contains a large proportion of the glyceride of valeric acid, besides monatomic ethers.	—

XII. SPERMACETI GROUP. WAXES.

Kind of wax	Source of wax	Specific gravity		Melting-point; ° C.	Solidifying-point; ° C.	Percentage of KHO for saponification		Chief chemical constituents			Other characters
		At 15° to 16°C.	At 98° to 99°C.			By free acid	Total	Free acids	Alcohols	Ethers or 'Esters'	
Spermaceti.	Deposits from oil of the sperm whale and allied *Cetacea*.	·942 to ·946	·808 to ·812	43 to 49	43 to 48	none or traces	12·8	None or traces .	—	Cetyl palmitate and its homologues.	White; highly crystalline. When saponified yields a palmitate and solid cetyl alcohol, $C_{16}H_{33}.OH$, and homologues extracted by ether from saponified liquid. Used in pharmacy, confectionery, and for candle-making.
Beeswax .	The honey-comb of various species of *bee*.	·959 to ·969 usually ·963 to ·966	·819 to ·829	62 to 64	60 to 62	2·0	9·3 to 9·6	Cerotic acid, $HOC_{27}H_{53}O$; 12 to 15 p.c.	—	Myricyl palmitate and a little palmitin, &c.	Yellow, peculiar smell. When bleached, white. Waxy lustre and fracture. Used for candle-making, moulding, &c. Adulterated with tallow, stearin, paraffin, resin, and other waxes.
Pe-la, Paila, or Chinese wax.	Produced by a species of *Coccus* which punctures the twigs of certain trees.	—	·809 to ·811	81 to 83	80 to 81	trace	6·3	—	—	Ceryl cerotate and homologues.	Snow-white, highly crystalline, brittle; called from its appearance 'vegetable spermaceti.' Often adulterated; frequently contains 15 to 20 p.c. of water.
Opium wax.	Capsules of *Papaver somniferum*.	—	—	79 to 82	76 to 80	—	—	—	—	Ceryl cerotate, and ceryl palmitate.	White, crystalline. Soluble in boiling chloroform.
Palm wax .	Bark of *Ceroxylon andicola* of the Cordilleras of New Granada.	—	—	72 to 86	—	—	—	—	—	—	Much resembles carnaüba wax. Slightly soluble in boiling alcohol.
Carnahuba, Carnaüba, or Brazil wax.	From the leaf covering of *Copernicea cerifera* of South America.	·995 to 1·000	·842	83 to 88	81 to 82	·4 to ·8	8·3 to 8·8	Cerotic acid, $HOC_{27}H_{53}O$; 3 to 6 p.c.; and traces of homologues.	Myricyl alcohol $C_{30}H_{61}OH$ and a little ceryl alcohol.	Myricyl cerotate, and allied esters.	Very hard, sulphur-yellow or yellowish-green. Not readily bleached without change. Used in candle-making, soap-making, and for adulterating beeswax. Highly complex composition (*v.* H. Stürke, A. 223, 283).
Ocuba wax .	Fruit stones of a *Myristica* growing in Para and Guiana.	—	—	36	—	—	—	—	—	—	Yellowish white. Soluble in boiling alcohol.

haviour of the oil with solvents, the rise of temperature with sulphuric acid, the elaïdin and sulphur chloride tests, and certain colour reactions.

Refraction of oils. Various instruments have been devised for differentiating oils by observing their refractive power, but in most cases they are ill-adapted for practical use, and are limited in their application to oils liquid at the ordinary temperature. An instrument in which this objection is overcome is the oleo-refractometer of Amagat and F. Jean (C. R. 109, 616; An. 15, 85). The oil to be observed is introduced into a hollow prism, which is immersed in a vessel with parallel sides filled with a standard oil. If the refractive power of the sample is the same as that of the standard oil no deviation of the ray of light which is caused to traverse the apparatus will take place; but otherwise deviation will occur in a direction and to an extent which can be seen and measured on a micrometer scale placed in the eye-piece of the telescope with which the instrument is furnished. As the angle of the prism, the neutral or standard oil, and the divisions of the scale are all arbitrary, the indications of the instrument are of limited value, but the following figures show the differences observed by F. Jean when various oils were compared, and they suffice to indicate the general results and possible applications of the method of observation:—

—	At 22°C.	At 45°C.
Standard or neutral oil	0°	0°
Almond oil . . .	+ 6°	—
Olive oil . . .	+1 to 2°	—
Earthnut oil. . .	+4·5°	—
Colza oil . . .	16·5° to 17·5°	—
Sesamé oil . . .	+17°	—
Cotton-seed oil . .	+ 20°	—
Poppy oil . . .	+ 30 to 34°	—
Linseed oil . . .	+53°	—
Hemp-seed oil . .	+33	—
Margarine (average) .	—	−15°
Butter fat . . .	—	−35°
Lard	—	−12·5°
Beef tallow . . .	—	−16°
Mutton tallow . .	—	−20°
Paris tallow . . .	—	−17°
La Plata tallow . .	—	−19°
Veal fat . . .	—	−19°
Horse fat . . .	—	−12°
Neatsfoot oil . .	—	−3°
Oleic acid from tallow or palm oil . .	−34 to −38°	—
Oleic acid from wool fat	+25°	—
Linoleic acid . .	+25°	—

F. Jean states that the apparatus is available for the estimation of methyl and amyl alcohol in spirit, of petroleum products in turpentine and benzene, &c.

J. Muter (An. 16, 88) has shown that the oleo-refractometer may be applied to the detection of cocoanut oil in butter if the indications are considered in conjunction with Reichert's volatile acid test.

Relations of fatty oils to solvents. Fatty oils are without exception wholly insoluble in *water* and *aqueous liquids*. In cold *alcohol* the liquid oils are, as a rule, but little soluble, and the solid fats and waxes still less so. In boiling alcohol some of the liquid oils dissolve to a considerable extent, especially if the solvent be anhydrous.

The drying oils are more soluble than the non-drying, and oils containing the glycerides of lower fatty acids (*e.g.* butter fat, cocoanut oil, porpoise oil) are exceptionally soluble in alcohol. Castor and croton oils dissolve with facility in alcohol, and are sharply distinguished by this character from the majority of oils. On the other hand, castor oil is practically insoluble in *petroleum spirit* and other petroleum products, with which most other fixed oils are miscible in all proportions. In *ether*, *chloroform*, *carbon disulphide*, *benzene*, and oil of *turpentine*, the fixed oils dissolve with great facility.

Many of the fatty oils dissolve with more or less facility in *glacial acetic acid*, and under certain conditions their behaviour is of value as a test; 3 c.c. of the oil, previously melted if necessary, should be treated in a test-tube with an equal measure of glacial acetic acid. The mixture is then gradually heated with continuous shaking until complete solution takes place or the acid begins to boil. The liquid is then allowed to cool slowly while constantly stirred with a thermometer, and the temperature noted at which a permanent turbidity appears. The test, which was first proposed by E. Valenta (D. P. J. 252, 296), has its indications disturbed by very slight variations in the strength of the glacial acetic acid, the specific gravity of which is an insufficient indication of strength. Hence all observations must be checked by concurrent tests made with the same acid on oil of known purity. The test furnishes a marked distinction between butter-fat and margarine, while rape oil and other oils from the *Cruciferæ* are incompletely soluble even at the boiling-point of the acetic acid.

Temperature-reactions of oils with sulphuric acid. When a fatty oil is mixed with strong sulphuric acid, an evolution of heat invariably occurs, and, if the experiment be made under certain definite conditions, the rise of temperature is approximately constant for the oil in question. The test was first suggested by Maumené (C. R. 35, 572) and is best performed in the manner recommended by L. Archbutt:—50 grams weight of the oil is placed in a 7 oz. beaker, and the latter immersed in a capacious vessel of water, together with the bottle of strong sulphuric acid, until they are both at the same temperature, which should not be far from 20°C. The beaker containing the oil is then wiped, and placed in a cotton-wool nest, previously made for it in a cardboard drum or a wider beaker. The immersed thermometer is then observed, and the temperature recorded. 10 c.c. of the concentrated sulphuric acid should then be withdrawn from the bottle with a pipette, and allowed to run into the oil. During the addition of the acid, which should occupy about one minute, the mixture must be constantly stirred with the thermometer, and the agitation continued till no further rise of temperature ensues. This point is readily observed, as the indication remains constant for a minute or two, and the temperature then begins to fall.

It is of the first importance that the acid used should be of full strength (not below 97 p.c. of H_2SO_4). The specific gravity is not sufficient evidence of this, for Lunge and Naef have shown that acid of 96 and of 99 p.c., and even of 95 and 100 p.c., have almost exactly the same density. Hence the strength should be ascertained by careful titration with standard alkali.

In the case of linseed oil and some fish oils, the reaction with sulphuric acid is so violent as to render loss probable, unless the experiment be carefully conducted. In such cases, dilution of the sample with an equal weight of olive or lard oil will suffice to bring the reaction within bounds (*v.* Ellis, S. C. I. 5, 150).

The following table shows the results usually obtained by Maumené's test. Other figures are given on pages 40 and 41.

Kind of oil	Rise of Temperature with sulphuric acid ; °C.					
	Maumené	Baynes	Dobb	Archbutt	Allen	Wiley
Olive oil . . .	42	40	39-43	$38\frac{1}{2}$–45	41–43	—
Almond oil . . .	52-54	35	—	—	—	—
Rape and colza oil .	57-58	60–92	54–60	54-64	51-60	—
Earthnut oil . .	67	—	—	47–60	—	69
Beechnut oil . .	65	—	—	—	—	—
Cotton-seed oil; crude .	—	84	61	70	67–69	79
,, ,, refined	—	77	—	75–76	74–75	—
Oleic acid . . .	—	—	—	$37\frac{1}{2}$	$38\frac{1}{2}$	—
Cocoanut olein . .	—	—	—	—	26–27	—
Castor oil . . .	47	—	—	46	65	—
Lard, pure . . .	—	—	—	—	—	41
Lard oil . . .	—	—	—	—	41	54
Tallow oil . . .	41–4	—	—	—	—	—
Neatsfoot oil . .	—	—	—	43	—	—
Horsefoot oil . .	51	—	—	—	—	—
Compounded lard. .	—	—	—	—	—	46–57

A valuable improvement in the mode of expressing the results of Maumené's temperature reaction has been made by Thomson and Ballantyne (S. C. I. 10, 233). It consists in ascertaining the rise of temperature produced by mixing 50 grams of water with 10 c.c. of strong sulphuric acid in the same vessel and under precisely the same conditions as those used for testing the oil. The rise of temperature with water is taken as 100, when the *specific temperature reaction* of the oil is obtained by the proportion:

$$\frac{\text{rise of temperature with oil multiplied by 100}}{\text{rise of temperature with water}} = \left\{\begin{array}{l}\text{spec.}\\ \text{temp.}\\ \text{reaction.}\end{array}\right.$$

The method possesses the great advantage that almost identical results are obtained with acids of somewhat different strengths (provided they are at least 95 p.c.), and hence the figures are much sharper and more distinctive. The following are the specific temperature reactions for various oils as observed by Thomson and Ballantyne:—

Oil	Temperature (Water=100)	No. of samples
Olive . .	89 to 95	11
Earthnut . .	105 to 137	2
Rape . .	125 to 144	5
Cotton-seed .	163 to 170	3
Linseed . .	270 to 349	4
Castor . .	89 to 92	2
Whale . .	157	1
Seal . . .	212 to 229	4
Cod . . .	243 to 272	3
Menhaden .	306	1
Sperm . .	93 to 100	2

Elaïdin reaction. When oleic acid is treated with nitrogen trioxide or an equivalent mixture, it is gradually changed into the isomeric body *elaïdic acid*, which is solid at ordinary temperatures. The glyceride of oleic acid undergoes a similar transformation with production of the solid isomer elaïdin, as also do such oils as consist of true olein in a state of approximate purity. On the contrary, the drying oils are not visibly affected by nitrous acid.

The proportion of the isomerising reagent requisite to produce the change and the influence of the proportion used on the rapidity and completeness of the reaction are almost unknown. No really scientific study of the formation of elaïdic acid or elaïdin appears to have been attempted, except some recent experiments by Finkener made in the laboratory of the Imperial Board of Trade at Berlin (Chem. Zeit. 10, 1039).

Of the various methods of obtaining the elaïdin reaction, the following, due to Poutet and L. Archbutt, is one of the best in practice. It depends on the remarkable power of retaining nitrous acid possessed by a solution of mercurous nitrate.

1 c.c. of mercury should be dissolved in 12 c.c. of cold nitric acid of 1·42 sp.gr. 2 c.c. of the freshly-made *deep-green* solution is then shaken in a wide-mouthed stoppered bottle with 50 c.c. of the oil to be tested, and the agitation repeated every ten minutes during two hours. When treated in this manner, oils consisting of approximately pure olein, or of mixtures of olein with the solid glycerides such as palmitin and stearin, give a solid product of greater or less consistency. Olive oil is remarkable for the canary or lemon-yellow colour and

great firmness of the elaïdin yielded by it. After twenty-four hours, the hardness of the product is such that it is impervious to, and sometimes rings when struck with, a glass rod, but this character is also possessed by the elaïdins yielded by arachis and lard oils. In making the elaïdin test, it is important to note the *time* required to obtain a 'solid' product, which will not move on shaking the bottle, as well as its ultimate consistency. Also the temperature should be kept as nearly as possible at 10°C., and not allowed to exceed 15°, or very erratic results may be obtained.

The behaviour of the more important liquid fixed oils, when tested in the foregoing manner, is as follows :

a. A solid, hard mass is yielded by olive, almond, earth-nut, lard, sperm, and sometimes neatsfoot oil.

b. A product of the consistence of butter is given by neatsfoot, bottlenose, mustard, and sometimes by earthnut, sperm, and rape oils.

c. A pasty or buttery mass which separates from a fluid portion is yielded by rape (mustard), sesamé, cotton-seed, sunflower, niger seed, cod-liver, seal, whale, and porpoise oils.

d. Liquid products are yielded by linseed, hemp-seed, walnut, and other drying oils.

In practice, the elaïdin-test receives its most important application in the assay of olive oil, with which it gives a very characteristic reaction.

Reaction of oils with chloride of sulphur. The vegetable drying oils are converted on treatment with sulphur chloride (S_2Cl_2) into gelatinous or elastic masses, which are employed as substitutes for indiarubber. T. P. Bruce Warren has investigated the reaction with a view to its employment in the analysis of oils. The effect of the treatment with sulphur chloride appears to vary materially with the proportion of the reagent used, which is usually 1 c.c., mixed with 1 c.c. of carbon disulphide, to 5 grams of the sample, to which 2 c.c. of carbon disulphide has been previously added. The mixture is heated on the water-bath till constant in weight, when the product is broken up as completely as possible and exhausted with carbon disulphide, the solution obtained being evaporated to dryness and the residue weighed. The various fixed oils are said to give constant and characteristic weights of the original dry product, of which definite amounts are dissolved by subsequent treatment with carbon disulphide; but, except in a few cases, these figures have not been published, and it does not appear that a mixture of two oils behaves in a manner which can be predicated from the nature of its constituents. Lard oil, and other animal oils, including fish oils, are stated not to yield solid products with chloride of sulphur; and the same is the case with cocoanut oil and the free fatty acids from any source. Blown or oxidised oils give black products. Warren claims that the method is available for the determination of vegetable oils in butter and lard, of lard and cotton-seed oils in olive oil, &c. For further details the original papers must be consulted (C. N. [56] 222, 231, 243, 262; [57] 26, 43, 113; [58] 4, 15; [62] 27, 51, 125, 215, 251).

Colour-reactions of oils. Many fatty oils give, when treated with chemical reagents, products which are often strongly coloured. To a certain extent these colour-reactions are characteristic of the oils by which they are produced, and hence may be employed for their identification. It must be borne in mind, however, that the albuminous, resinous, and other foreign matters, on the presence of which the colour-reactions in most cases depend, are more or less completely removed or modified by the process employed for refining the oil. Hence, considerable variation is observed in the behaviour of different samples of oil with the same reagent, and the value of the reactions is still further reduced by the modifications produced by the presence of free fatty acids in the oils. Still less are the indications to be trusted when mixed oils are under examination.

The colour-reactions of oils with *nitric acid* are sometimes characteristic, especially in the case of seed oils. The test is recommended to be applied in various ways, but perhaps those methods which combine observations of the colour and the character of the elaïdin are to be preferred. Thus O. Bach agitates 5 c.c. of the sample with an equal measure of nitric acid of 1·30 sp.gr. After noting any colouration the mixture is immersed in boiling water for five minutes, and the effect again observed. A more or less violent reaction often occurs on heating, even resulting, in the case of cotton and sesamé oils, in the mixture being projected from the tube.

Bach gives the following table of results :—

Kind of oil	After agitation with nitric acid	After heating for five minutes	After standing 12 to 18 hours
Olive	Pale green . . .	Orange-yellow . .	Solid
Earthnut . . .	Pale rose . . .	Brownish-yellow .	Solid
Rape	Pale rose . . .	Orange-yellow . .	Solid
Sesamé . . .	White	Brownish-yellow . .	Liquid
Sunflower . . .	Dirty white . .	Reddish-yellow . .	Buttery
Cotton-seed . .	Yellowish-brown . .	Reddish-brown . .	Buttery
Castor . . .	Pale rose . . .	Golden-yellow . .	Buttery

A similar test has been described by Massie, who agitates 10 grams of the oil with 5 of nitric acid (sp.gr. 1·40) and 1 gram of mercury, and observes the colour of the product after one hour, and also the time required for solidification. Thus :—

Oil	Colouration	Minutes for solidification
Olive	Pale yellowish-green	60
Hazelnut	White	60
Almond	White	90
Earthnut	Pale reddish	105
Apricot	Rose	105
Rape	Orange	200
Cotton-seed	Orange-red	105
Sesamé	Yellowish-orange	150
Beechnut	Reddish-orange	360
Poppy	Red	Fluid
Camelina	Reddish-orange	Fluid

In employing colour-tests for oils, it is very desirable to examine specimens of oils of known purity side by side with the sample, instead of trusting implicitly to printed descriptions of reactions.

The following table by A. H. Allen shows the effect produced on placing a drop or two of *strong sulphuric acid* in the centre of about twenty drops of the oil, and observing the colour both before and after stirring:—

Oil	1 or 2 drops of strong sulphuric acid to 20 of the oil	
	Before stirring	After stirring
Vegetable oils—		
Olive oil	Yellow, green, or pale brown	Light brown, or olive green
Almond oil	Colourless, or yellow	Dark yellow, olive, or brown
Earthnut oil	Greyish yellow to orange	Greenish, or reddish-brown
Rape oil, crude	Green, with brown rings	Bright green, turning brownish
„ refined	Yellow, with red or brown rings	Brown
Mustard oil	Dark yellow, with orange streaks	Reddish-brown
Cotton-seed oil, crude	Very bright red	Dark red, nearly black
„ refined	Reddish-brown	Dark reddish brown
Niger-seed oil	Yellow, with brown clot	Reddish or greenish-brown
Poppy-seed oil	Yellow spot, with orange streaks or rings	Olive or reddish-brown
Linseed oil, raw	Hard-brown, or greenish-brown clot	Mottled, dark brown
„ boiled	Hard-brown clot	Mottled, dark brown
Castor oil	Yellow to pale brown	Nearly colourless, or pale brown
Animal oils—		
Lard oil	Greenish yellow, or brownish with brown streaks	Mottled or dirty brown
Tallow oil	Yellow spot, with pink streaks	Orange red
Whale oil	Red, turning violet	Brownish-red, turning brown or black
Seal oil	Orange spot, with purple streaks	Bright red, changing to mottled brown
Cod-liver oil	Dark-red spot with purple streaks	Purple, changing to dark brown
Sperm oil	Pure-brown spot, with faint yellow ring	Purple, changing to reddish or dark brown
Hydrocarbon oils—		
Petroleum lubricating oil	Brown	Dark brown, with blue fluorescence
Shale lubricating oil	Dark reddish-brown	Reddish-brown, with blue fluorescence
Resin oil, brown	Bright mahogany brown	Dark brown, with purple fluorescence
„ pale	Mahogany brown	Red-brown with purple fluorescence

As already stated, the colours produced by different samples of the same kind of oil when treated with strong sulphuric acid are liable to considerable variation, in addition to which the reactions are in some cases complicated or rendered indistinct by the charring action exerted by the acid. This may be avoided by dissolving one drop of the oil in twenty of carbon disulphide, and agitating the solution with a drop of strong sulphuric acid. Whale oil when thus treated gives a fine violet colouration, quickly changing to brown, whereas with sulphuric acid alone a mere red or reddish-brown colour changing to black or brown is usually obtained.

Systematic methods of examining oils have been described by various chemists, but no such method can be implicitly relied on, owing to the variable nature of the oils themselves. In particular, any positive recognition based on the colour-reactions of an oil is of little value, unless confirmed by the indications of other tests.

In examining oils for the detection of adulteration, the relative commercial value of the different kinds should never be lost sight of, and it must be remembered, that in addition to the adulteration of the more valuable fatty oils with the cheaper, their sophistication by admixture with the hydrocarbon oils obtained by the distillation of petroleum, shale, coal, resin, &c., is also extensively practised.

The following is a list of the principal commercial fluid oils, arranged as nearly as possible in the order of their usual value, which in some cases is liable to considerable fluctuations:—

1. Olive oil
2. Sperm oil
3. Neatsfoot oil
4. (a) Bottlenose oil
   (b) Lard oil
   (c) Castor oil
7. Cod oil
8. Rape or Colza oil
9. (a) Arachis oil
   (b) Sesamé oil
   (c) Poppy-seed oil
12. Seal oil
13. Niger-seed oil
14. Linseed oil
15. Whale oil
16. Cotton-seed oil
17. Menhaden oil
18. Japan fish oil
19. Mineral oil
20. Resin oil

Practically it is of less importance to know whether an oil has the origin attributed to it than to learn whether its characters are such as will allow it to be safely used as a substitute for the genuine oil.

Although it is not possible to lay down any general scheme which shall be available for the identification of any unmixed fatty oil, the recognition is much facilitated by conducting the examination on a systematic plan. The following mode of procedure is recommended:—

1. Place a drop of the oil on the back of the tongue by means of a glass rod, and taste it carefully, avoiding too hasty a decision. In this manner marine animal oils, linseed oil, croton oil, mineral oil, resin oil, and some others may generally be detected. Resin oil is remarkable for the nauseous after-taste of resin produced by it. Rancidity of an oil may easily be recognised by the taste.

2. Heat a portion of the oil in a porcelain or platinum capsule to about 140° or 150°C. and observe the odour carefully. When sufficiently cool, pour a little of the oil into one hand, rub with the other, and smell again. A little practice will allow of vegetable oils being readily distinguished from animal oils, and the products of fish and marine mammals from those of terrestrial animals. The odour on heating will also frequently permit the recognition of mineral and resin oils, and, if the remainder of the oil be strongly heated till it ignites and the flame then blown out, the vapours will often have a highly characteristic odour.

3. Ascertain the sp.gr. of the sample at 15·5°C. (60°F.) if fluid at that temperature, but at the boiling-point of water if solid at the ordinary temperature.

Oils, liquid at the ordinary temperature (15–16°*C*.), *arranged according to their specific gravity.*

Class of oil	Sp.gr. at 15° to 16°C. (=59° to 61°F.)				
	a. ·875 to ·884	*b.* ·884 to ·912	*c.* ·912 to ·920	*d.* ·920 to ·937	*e.* ·937 to ·967
Vegetable oils . .	None . .	None . .	Olive Almond Earthnut Rape or colza Mustard } Non-drying oils (p. 40)	Cotton-seed Sesamé Sunflower Hazelnut Poppy Hemp-seed Linseed (raw) Walnut } More or less drying oils (p. 40)	Japanese wood Croton Castor Boiled linseed Blown oils
Terrestrial animal oils	None . .	None . .	Neatsfoot Bone Lard oil Tallow oil	None . . .	None
Marine animal oils .	Sperm Doegling (Bottlenose)	None . .	None . . .	Whale Porpoise Seal Menhaden Cod-liver Shark-liver	None
Free fatty acids .	None . .	Oleic acid .		Linoleic acid .	Ricinoleic acid
Hydrocarbon oils .	Shale products Petroleum products	Shale products Petroleum products	Heavy petroleum products	Heavy mineral oils	None

The hydrocarbon oil produced by the distillation of resin is not included in these tables, as its high density (·970–1·000) places it outside any of the classes. The same remark applies to resin itself, which is somewhat denser than water, and to the high-boiling coal-tar products which might be mistaken for or found mixed with the fixed oils. More precise statements of the sp.grs. of fatty oils are given on page 28.

The sample having been satisfactorily classified by means of its taste, smell, melting-point, and density, the subsequent means of identification depend on the result of these tests.

a. Sperm and *bottlenose oils* are readily distinguished from *shale* and *petroleum products* of similar density by the elaïdin test, the determination of their saponification-equivalents, and the quantitative results of their saponification.

b. Oleic acid is sharply distinguished from *hydrocarbon oils* by its solubility in an aqueous solution of caustic soda. Mixtures of oleic acid and hydrocarbons may be accurately analysed by titration with standard alkali and phenolphthaleïn. If glycerides or sperm oil be present in addition, the mixture should be analysed as indicated on page 22.

Oils &c. which are pasty or solid, at ordinary temperatures (15–16°C.), *arranged according to their specific gravities when melted.*

Class of oil	Sp.gr. at 98° to 100°C.			
	f. ·750 to ·800	*g.* ·800 to ·855	*h.* ·855 to ·863	*i.* ·863 to ·876
Vegetable fats	None	None	Palm oil Cacao butter	Palmnut oil Cocoanut oil Japan 'wax' Myrtle 'wax' Cotton-seed stearin
Animal fats	None	None	Tallow Lard Suet Dripping Bone fat Margarine	Butter fat Compounded lard
Waxes	None	Spermaceti Beeswax Chinese wax Carnaüba wax	None	None
Free fatty acids	None	Stearic acid Palmitic acid Oleic acid	None	None
Hydrocarbons	Paraffin wax Ozokerite	Shale and petroleum products	Vaseline	

c. The *non-drying vegetable oils* are distinguishable from the similar oils of animal origin by their taste and odour on heating. The melting-points of the fatty acids from the animal oleins are much higher than those prepared from the vegetable non-drying oils, while their iodine absorptions are usually lower. Many of the vegetable oils show banded absorption-spectra, which is never the case with animal oils. The vegetable non-drying oils may be distinguished from each other by careful observations of their density, viscosity, absorption-spectra, and the rise of temperature produced by sulphuric acid. The elaïdin reaction and colour tests with sulphuric and nitric acids are sometimes useful as confirmatory tests. *Rape* and *mustard oils* are distinguished from the rest by their insolubility in an equal measure of glacial acetic acid at 100°, and by their high saponification-equivalents. The *animal oils* of the group may be distinguished from each other by their odour, viscosity, and melting-points, and to some extent by their reactions with concentrated sulphuric acid and the elaïdin-test. Bone oil usually gives an orange or reddish-yellow elaïdin of a pasty consistency, while lard (and tallow) oil yields a very firm product of a pale or lemon-yellow colour. The product from neatsfoot oil is variable.

d. The *vegetable oils* possessing more or less well-defined *drying characters* may be in a great measure differentiated by their densities and viscosities. The elaïdin-test and colour-reactions furnish further means of identification, and the results may, when necessary, be supplemented by determinations of the solubility in glacial acetic acid, of the rise of temperature with sulphuric acid, of the iodine-absorption, and of the melting and solidifying points of the fatty acids obtained by saponifying the oil. The figures ordinarily yielded by those methods of examination are expressed in the following table:—

Oil	Turbidity-temperature (Valenta)	Temperature with H_2SO_4 (Maumené)	Iodine absorption (Hübl)	Fatty acids (Hübl)	
				Melting-point	Solidifying-point
Cotton-seed	87 to 110	67 to 75	105 to 109	37·7	30·5
Sesamé	87 to 107	67 to 70	103 to 108	26·0	22·3
Niger seed	49	81 to 82	103	26·0	—
Poppy-seed	—	86 to 88	134 to 137	20·5	16·5
Hemp-seed	—	98	143	19·0	15·0
Linseed	57	103 to 111[1]	155 to 160[1]	17·0	13·3
Walnut	—	101	142 to 144	20·0	16·0

[1] The rise of temperature and iodine-absorption for linseed oil found by Thomson and Ballantyne (S. C. I. 10, 233) are considerably above the figures recorded in the table.

The fatty acids from the moderately drying oils, especially cotton-seed oil, solidify at a much higher temperature than those from the strongly drying oils, and the same distinction applies, though in a less marked manner, to the oils themselves.

The colour-tests with sulphuric and nitric acids (pages 37, 38) afford useful confirmatory evidence of the identity of seed oils, and their reaction with chloride of sulphur is also of service.

Cotton-seed oil can be recognised with tolerable certainty by its characteristic behaviour with nitrate of silver, whereby as little as 5 p.c. in olive oil or lard may be detected. This test, originally due to E. Milliau, is applied by M. Conroy in the following improved manner:—5 grams of silver nitrate and 1 of nitric acid (sp.gr. 1·42) are dissolved in 100 c.c. of rectified spirit (sp.gr. ·838). Five c.c. of the oil or melted and filtered lard is treated with 1 c.c. of this solution, and the test-tube immersed in boiling water for five minutes. In presence of cotton-seed oil the liquid assumes an olive-brown colour, intense in accordance with the proportion present.

Sesamé oil gives a characteristic colour-reaction by which it can be detected in olive oil with ease and certainty. The oil is agitated for 10 minutes with half its measure of fuming hydrochloric acid, to which a little cane-sugar has been added. On separating from the oil, if the sample contained sesamé oil the acid liquid will be found to have a rose tint, or even the colour of permanganate solution. To avoid certain sources of error, Milliau recommends that the test should be made on the fatty acids from the oil; but such a plan greatly diminishes the delicacy of the reaction. Sesamé oil is stated to give a fine green colouration when treated with a mixture of equal parts of strong nitric and sulphuric acids.

Cocoanut olein is distinguished from other fluid vegetable oils by its low saponification equivalent, and the very moderate rise of temperature (37°C.) which occurs on treating it with sulphuric acid. It is not solidified by chloride of sulphur.

The *marine animal oils* may be distinguished as a class by their fishy smell and taste; by the red or reddish-brown colour obtained on saponifying them; and by the darkening that ensues on passing a current of chlorine through the oil. They may be differentiated by their saponification-equivalents, behaviour with acetic acid, rise of temperature with strong sulphuric acid, and their iodine and bromine absorptions. The last determinations have been made by Mills, and if his figures are multiplied by $\frac{127}{80}$, the corresponding (calculated) iodine absorption is obtained (with fair accuracy in some cases, but in others the discrepancy is very wide.

The colour-test with sulphuric acid gives further useful information. Porpoise oil and some varieties of whale oil contain a notable proportion of glycerides of lower fatty acids, and hence give very sensible quantities of volatile fatty acids when the solution of the saponified oil is acidulated with dilute sulphuric acid and distilled.

The following table shows the behaviour of the principal fish oils with the foregoing tests. For convenience of comparison, sperm and bottlenose oils are included in the table.

Oil	Saponification equivalent	Turbidity-temperature	Temperature with H_2SO_4	Halogen-absorption	
				Bromine	$\times \frac{127}{80}$ = Iodine
Sperm . . .	380 to 454	98	45 to 47	56	89
Bottlenose . . .	419 to 456	102	41 to 47	49	78
Whale. . . .	250 to 296	47	85 to 91	51	81
Porpoise . . .	256 to 260	40	50	—	—
Seal	286 to 296	-	92	57 to 60	91 to 95
Menhaden . . .	292	64	123 to 128	—	—
Cod-liver . . .	303	79 to 101	103 to 116	81 to 87	129 to 138
Ling-liver . . .	—	—	—	82	131
Skate-liver . . .	-	—	102	109 to 123	173 to 195
Shark-liver . . .	327 to 400	105	90	84	134

A mixture of strong sulphuric and nitric acids, used in the proportion of 1 drop to 10 of the oil, has been proposed by H. Meyer as a colour-test for certain fish oils. Allen gives the following description of the reactions obtained with this test:—

Oil	Sp.gr. of sample	Before stirring	After stirring
Cod-liver . .	·9290	Violet quickly becoming rose-red.	Rose-red, changing to light brown.
Hake-liver . .	·9270	Dark violet, changing to dark brown.	Brownish violet, changing to light brown.
Skate-liver . .	·9327	Light violet, changing to brown	Brownish violet, changing to brown.
Shark-liver . .	·9285	Light brown with spots of red	Light brown, becoming darker
Herring . .	·9326	Brown	Darker brown.
Sprat . . .	·9284	Light brown	Unchanged.
Seal . . .	·9245	Light brown	Lemon-yellow, rapidly changing to emerald-green and bluish-green.
Whale . .	·9301	Light brown	Darker.

e. The oils of a density exceeding ·937 are few in number, and easily distinguished. *Croton* and *castor oil* are purgative, and readily soluble in rectified spirit, but have little further resemblance. *Boiled linseed oil* and *Japanese wood oil* have a density between ·937 and ·950, dry very rapidly on exposure, and give a firm brown or black clot with sulphuric acid. Blown oils closely resemble castor oil, but may be readily distinguished as described on page 25. *Rosin oil* has a density exceeding ·970, and is not saponified to any considerable extent by alkalis. It is readily identified by its strong after-taste, and the terebinthinous odour developed when the sample is heated till it catches fire, and the flame then blown out.

f and *g*. The distinctions between the various *waxes* are fully indicated in the table on p. 34. Free fatty acids are at once distinguished from the waxes by their solubility in alcohol, behaviour with alkalis, and their saponification equivalents; from each other by their melting-points and combining weights. Paraffin wax, ozokerite, vaseline, and similar *hydrocarbons* are sharply distinguished from the waxes and fatty acids by being incapable of saponification.

h. The *solid vegetable fats* of low density are somewhat numerous and have not been much studied, but very few of them are commonly met with. The colour, taste, and odour suffice to distinguish many of them, and further information is afforded by their behaviour with glacial acetic acid and the determination of their melting and solidifying points. The animal fats may be distinguished by similar means.

i. The vegetable fats of high density are readily differentiated. *Cocoanut* and *palm-nut oils* are soft, melt very readily, and have low saponification equivalents. *Japan* and *myrtle wax* are hard wax-like bodies of comparatively high melting-point, but are true fats and not waxes, as they yield glycerin instead of solid monatomic alcohols when saponified. Palm-nut oil is distinguished from cocoanut oil by its taste and smell. *Butter fat* is the only fat of animal origin (except wool fat) having a density higher than ·863. Its odour, taste, and yield of soluble volatile acids when the saponified substance is distilled with dilute sulphuric acid are highly characteristic.

In the case of a sample consisting of a *complex mixture of wholly unknown oils*, the identification of the constituents is often a problem of extreme difficulty, but when the leading component is known or can be recognised the detection of the others becomes more feasible. It must, however, always be borne in mind that in most cases oils cannot be recognised by distinct and specific tests, such as exist for the different metals, and that in arriving at a conclusion as to the composition of any sample of mixed oils the analyst must be content to be guided in a great measure by circumstantial evidence and a careful consideration of probabilities.

The following facts, which depend on the chemical nature of the oil, are of importance in the examination of complex samples, and to a less extent for the identification of unmixed oils.

Much information may be obtained by saponifying the oil and determining the products formed by the reaction. Thus most fixed oils are split up into a fatty acid and glycerin, but sperm oil and the waxes yield products differing from glycerin in being insoluble in water but soluble in ether. Sperm and bottlenose oils only yield about 63 p.c. of fatty acids, while most other fixed oils (not the waxes) give about 95 p.c. Butter-fat, porpoise oil, and the oils from cocoanut and palm-nut yield a notable proportion of acids which are volatile or soluble in water; but in the case of almost all other oils the whole of the fatty acids are practically insoluble. Resin gives 100 p.c. of resin acids and no glycerin, but mineral and resin oils do not undergo saponification at all, and so can be dissolved out of the solution of soap by agitating it with ether.

The physical properties and combining weights of the fatty acids afford important information. The acids from rape and castor oils neutralise sensibly less alkali than those from most oils. Lard, tallow, and neatsfoot oils yield fatty acids of much higher melting-point than the non-drying vegetable oils which they otherwise resemble. Cotton-seed oil yields fatty acids solid at the ordinary temperature, while most drying and semi-drying oils yield liquid acids. Any admixture of resin acids tends greatly to increase the density of the fatty acids, at the same time lowering their melting-point. When it is intended to examine the characters of the fatty acids it is highly important that the aqueous and alkaline solution of the soap should be previously agitated with ether until nothing more is removed, as any admixture of wax or hydrocarbon oil would profoundly modify the properties of the fatty acids.

The drying oils are heavier but less viscous than the non-drying oils, apparently in proportion to their drying tendency. The non-drying oils give solid elaïdin, the product becoming less and less firm as it is derived from a more strongly drying oil. Similarly the heating produced by mixture with sulphuric acid, the solubility in glacial acetic acid, the reaction with sulphur chloride, and the iodine-absorption appear to bear a direct relationship to the drying properties of a vegetable oil. By a careful application of these facts an approximate estimate of the proportions of different oils in a mixture can often be made.

HIGHER FATTY ACIDS.

Under the denomination of fatty acids used in its widest sense is included the whole series of homologous acids of which formic acid is the lowest member, together with the various homologous acids of the acrylic or oleic series, the peculiar acids obtained by the saponification of castor and drying oils, and many others.

The following tables give some particulars respecting such higher fatty acids as are of interest or importance as constituents of the fixed oils or fats. The members containing an even number of carbon atoms in the molecule appear to occur more commonly than the alternate acids of the series.

It will be noted that the acids of the stearic series become less fusible with an increase in the number of carbon atoms. Baeyer has shown, however, that the rise in the melting-point is not strictly regular, inasmuch as an acid of the stearic series containing an uneven number of carbon atoms always possesses a lower melting-point than the preceding member of the series containing an even number of carbon atoms. In a similar manner, the boiling-point of the acids of the stearic series rises with an increase in the number of carbon atoms. The higher members may be distilled without alteration under diminished pressure or in a vacuum, but when distilled under the ordinary atmospheric pressure they suffer decomposition. Similarly, oleic acid may be distilled in a vacuum, or in a current of superheated steam at 250°C., without material alteration,[1] but if distilled with contact of air, it is partially decomposed, with formation of carbon dioxide, paraffinoid hydrocarbons, and acetic, caproic, caprilic, capric, sebacic, and other acids.

In the following tables the acids of the different series are arranged together. Their relationship is evident from the following list of the acids containing 18 carbon atoms in the molecule:

$C_{18}H_{36}O_2$, stearic acid.
$C_{18}H_{34}O_2$, oleic acid; elaïdic acid.
$C_{18}H_{32}O_2$, linoleic acid; stearolic acid.
$C_{18}H_{30}O_2$, linolenic acid; isolinolenic acid.
$C_{18}H_{34}O_3$, ricinoleic acid; ricinosoleic acid; ricinelaïdic acid; rapic acid.

A.—*Higher Acids of the Acetic or Stearic Series*—$C_nH_{2n}O_2 = C_nH_{2n+1}.COOH$.

Formula	Name of acid	Chief source or mode of occurrence	Melting-point; °C.	Boiling-point under 100 mm. pressure	Other characters, &c.	Isomeric acids of interest
$C_8H_{16}O_2$	Caprilic .	As a glyceride in cocoanut oil, butter-fat, and Limburg cheese	16·5	—	Crystallises in needles or plates. Soluble in 400 parts of boiling water, mostly deposited on cooling, readily soluble in alcohol, ether, and benzene. Boils at 236°C. Ba salt moderately soluble	*Isoctoic acid*, obtained by oxidising isooctyl alcohol, is liquid at −17°, and boils at 219°
$C_9H_{18}O_2$	Pelargonic .	In geranium leaves, *Pelargonium roseum*, and as an ether in wine-lees. Also obtainable from oil of rue	12·5	—	Boils at 254°. Crystallisable. Ba salt very difficultly soluble in cold water	*Isononoic acid*, obtained synthetically. Not solid at −11°; boils at 245°
$C_{10}H_{20}O_2$	Capric .	As a glyceride in butter, cod-liver oil, and cocoanut oil. As an ether in fusel oil. Formed by fermentation of solution of suint	30·0	201·5	Boils at 268° to 270°C. Crystallises in brilliant plates. Faint goat-like odour. Slightly soluble in water, easily in alcohol and ether. Ba salt forms nacreous crystals, difficultly soluble in boiling water. Soluble in alcohol	*Isodecatoic acid*, obtained by oxidising isopentyl alcohol, is an oily liquid not solidified at −37°, and boiling at 241·5°. Ba salt is oily or waxy
$C_{11}H_{22}O_2$	Umbellulic acid	Obtained by synthetical methods, and occurs as a glyceride in chaulmoogra oil and fat of Californian bay tree	28·5	212·5	Crystalline scales. Faint odour resembling caproic acid; peculiar irritating taste. Boils at 270–275°, and distils unchanged	*Cocinic acid* exists as a glyceride in cocoanut oil, and has been obtained from spermaceti
$C_{12}H_{24}O_2$	Lauric .	As a glyceride in cocoanut and palm-nut oils, croton oil, laurel oil, pichurum beans, &c. As an ether in spermaceti	43·5	225·5	Distils readily with open steam. Solidifies from fusion in scales. Crystallises from alcohol in white needles. Pb salt insoluble in ether, sparingly in alcohol	—
$C_{13}H_{26}O_2$	Tridecatoic	Obtained by synthetical methods	40·5	236	Scaly, crystalline substance.	*Cocinic acid* (see above), not improbably contains $C_{13}H_{26}O_2$
$C_{14}H_{28}O_2$	Myristic .	As a glyceride in cocoanut oil, nutmeg butter, croton oil, dika-bread, &c. As an ether in spermaceti	53 8	248	Crystallises from alcohol in shining laminæ. Pb salt soluble in alcohol, insoluble in ether	—
$C_{15}H_{30}O_2$	Pentadecatoic	Obtained by synthetical methods	51·0	257	Pearly crystalline scales .	*Benomargaric acid*, from oil of ben, melts at 52–53° *Cetic acid*, from spermaceti *Isocetic acid*, from oil of *medicinier*, melts at 55° *Acid* from *Agaricus integer*, melts at 70° *Acid* from oxidation of cocceryl alcohol, melts at 59–60°

Cahours and Demarçay (C. R. 90, 156) found, in the product obtained by distilling the higher fatty acids in a current of superheated steam, all the lower acids of the acetic series, from formic to caprylic. Pelargonic and capric acids were also believed to be formed, as also traces of acids of the succinic series, and sebacic acid and its lower homologues.

A.—*Higher Acids of the Acetic or Stearic Series* (continued).

Formula	Name of acid	Chief source or mode of occurrence	Melting-point; °C.	Boiling-point under 100 mm. pressure	Other characters, &c.	Isomeric acids of interest
$C_{16}H_{32}O_2$	Palmitic .	As a glyceride in many or most natural fats, notably palm oil; as cetyl palmitate in spermaceti; as myricyl palmitate in beeswax. Free in adipocere. Principal constituent of commercial palmitin	62·0	268·5	White crystalline needles. Distils unchanged *in vacuo.* Pb salt insol. in ether; melts at 108–112°C.	*Iso-palmitic acid*, obtained by synthetical means, melts at 26–27°
$C_{17}H_{34}O_2$	Margaric .	Obtained by synthetical means. Said to occur in a free state in adipocere	59·9	277	Pearly crystalline scales, obtained by the action of alkalis on cetyl cyanide	*Daturic acid*, from thornapple seeds. Melts at 55° (C. R. 111, 305)
$C_{18}H_{36}O_2$	Stearic .	As a glyceride in admixture with palmitin in many natural fats. Principal component of commercial stearin	69·9	287	Forms nacreous laminæ or needles; sparingly soluble in cold alcohol. Pb salt melts at 125°C., and is insoluble in ether	*Iso-stearic acid*, or dioctyl-acetic acid, obtained by synthesis, melts at 38·5° *Cetyl-acetic acid*, melts at 63–64°
$C_{19}H_{38}O_2$	Nondecatoic	Obtained with margaric acid from crude cetyl cyanide	66·2	—	Scaly crystalline mass . .	—
$C_{20}H_{40}O_2$	Arachidic .	As a glyceride in earthnut oil, butter fat, &c.	75·0	—	Crystallises from hot alcohol in very small shining scales of pearly lustre. Insoluble in cold alcohol of ·880 sp.gr.	—
$C_{21}H_{42}O_2$	Medullic .	As a glyceride in beef marrow	72·5	—		—
$C_{22}H_{44}O_2$	Behenic .	As a glyceride in oil of ben and black mustard, and in small quantity in rape oil	76·0	—	Shining silvery plates, resembling stearic acid	—
$C_{23}H_{46}O_2$	Unknown .	—	—	—	—	—
$C_{24}H_{48}O_2$	Lignoceric.	Occurs in beechwood tar and earthnut oil	80·5	—	Crystallises from hot alcohol in interlaced needles. Pb salt insoluble in alcohol or ether.	*Paraffinic acid*, obtained by the oxidation of paraffin wax with fuming nitric acid, melts at 45–47°
$C_{25}H_{50}O_2$	Hyænic .	As a glyceride in the glandular pouches of the striped hyena; and in suint	77·5	—	Crystallises from hot alcohol in microscopic curved needles; from ether in more distinct crystals	*Acid* from carnaüba wax, melts at 72·5°
$C_{26}H_{52}O_2$	Geoceric .	Produced by distillation of brown coal	—	—	—	—
$C_{27}H_{54}O_2$	Cerotic .	In the free state in beeswax and carnaüba wax; as ceryl cerotate in Chinese wax and opium wax	81·5	—	Crystallises in small grains; soluble in hot alcohol or ether, but almost wholly deposited on cooling. Pb salt insoluble in alcohol or ether	—
$C_{28}H_{56}O_2$	Unknown .	—	—	—	—	—
$C_{29}H_{58}O_2$	Unknown .		—	—	—	—
$C_{30}H_{60}O_2$	Melissic .	Occurs in small quantity in beeswax	90	—	Obtained by fusing myricyl alcohol with potash. Crystallises in lustrous white plates or needles. Readily soluble in hot alcohol CS_2 &c., but only sparingly in boiling ether. Pb salt insoluble in alcohol or ether; melts at 118–119°	—
$C_{31}H_{62}O_2$	Unnamed .	By heating the myricyl alcohol from beeswax with soda-lime	88·5 89·0	—	White needles. Pb salt melts at 115–116°	—

B.—*Higher Acids of the Acrylic or Oleic Series*—$C_nH_{2n-2}O_2$, *or* $C_nH_{2n-1}.COOH$.

Formula	Name of acid	Chief source or mode of formation	Melting-point °C.	Other characters	Isomeric (or polymeric) acids produced by the action of nitrous acid on natural acids
$C_{15}H_{28}O_2$	Moringic acid	As a glyceride in oil of ben	0	Crystallisable. Existence is somewhat doubtful	—
	Cimicic acid .	Exists in liquid ejected by the grey-leaf bug (*Rhapigaster punctipennis*)	44	Crystallises from ether in prisms united in stellar forms, and is sparingly soluble in alcohol, readily in ether. Rancid odour	—

B.—*Higher Acids of the Acrylic or Oleic Series* (continued).

Formula	Name of acid	Chief source or mode of formation	Melting-point °C.	Other characters	Isomeric (or polymeric) acids produced by the action of nitrous acids on natural acids
$C_{16}H_{30}O_2$	Hypogæic acid	As a glyceride in the oil of the earthnut (*Arachis hypogæa*) and in lycopodium spores	33	Forms colourless crystals very readily soluble in alcohol and ether. Combines with Br_2. Yields gaïdic acid with nitrous acid and sebacic acid on distillation. Pb salt is soluble in ether	*Gaïdic acid* forms a crystalline mass melting at 39°. Volatilises almost unchanged; readily soluble in alcohol; combines with Br_2
	Physetoleic acid	As an ester in sperm oil	30	Differs from hypogæic acid in not yielding sebacic acid on distillation	*Physetelaïdic* acid. Produced by action of HNO_2 on physetoleic acid
$C_{17}H_{32}O_2$	Unknown	—	—	—	—
$C_{18}H_{34}O_2$	Oleic acid	As a glyceride in the majority of fatty oils. Forms the 'olein' of commerce	14	Crystallises from alcoholic solution in dazzling white needles. Insoluble in water, soluble in ether, oils, &c. Pb salt soluble in ether yields sebacic acid on distillation and elaidic acid with HNO_2. Combines with Br_2. Fused with KHO yields acetate and palmitate	*Elaïdic acid.* Produced by action of HNO_2 on oleic acid. Pearly plates melting at 45° and distilling almost unchanged
	Iso-oleic acid	By distillation of hydroxystearic acid	45	Soluble in alcohol and ether. Unites with Br_2. Behaves like oleic acid when fused with alkali	
	Aldepalmitic acid	From butter fat	—	Forms a solid compound with alcohol. Doubtful existence (S. C. I. 10, 212)	—
$C_{19}H_{36}O_2$	Doeglic acid	As an ester in bottlenose oil	16	Resembles oleic acid. Yields doeglaïdic acid with HNO_2	*Doeglaïdic acid*, produced by action of HNO_2 on doeglic acid
$C_{20}H_{38}O_2$	Unknown	—	—	—	—
$C_{21}H_{40}O_2$	Unknown	—	—	—	—
$C_{22}H_{42}O_2$	Erucic or brassic acid	As a glyceride in rape, grapeseed, and black and white mustard oils	33–34	Crystallises from alcohol in long, thin, lustrous laminæ or needles. Combines with Br_2. Pb salt very easily soluble in hot ether, acetone, or benzene. Yields erucaïdic acid with HNO_2 and acetate and arachidate when fused with KHO	*Erucaïdic or Brassaïdic acid.* Produced by action of HNO_2 on brassic acid. Melts at 56°. Pb salt is nearly insoluble in warm ether

C. *Higher Acids of the Propiolic or Linoleic Series*, $C_nH_{2n-4}O_2$.

Formula	Name of acid	Chief source or mode of occurrence	Other characters	Isomeric acids	
$C_{14}H_{24}O_2$	—	—	—	*Myristolic acid*, melts at 12°	Obtained by the action of alcoholic potash on the dibromo-acid of the acetic series containing the same number of carbon atoms; *e.g.* $C_{18}H_{34}Br_2O_2 + 2KHO = C_{18}H_{32}O_2 + 2KBr$
$C_{15}H_{26}O_2$	Pentadecinoic acid	—	—	—	
$C_{16}H_{28}O_2$	Linoleic acid	As a glyceride in poppy and hemp oils	See below	*Palmitolic acid*, melts at 42°; crystallises in needles	
$C_{17}H_{30}O_2$	Elæomargaric acid Elæolic acid	As a glyceride, together with that of its isomer elæolic acid[1] in the seeds of *Elæococcus vernicia*, which yields Japanese wood oil	—	—	
$C_{18}H_{32}O_2$	Linoleic or Homolinoleic acid	As a glyceride in cotton, hemp, and poppy oils, and less abundantly in linseed oil	Liquid at low temperatures. Not solidified by HNO_3. Yields stearic acid by hydrogenation, and *sativic acid* when oxidised in alkaline solution. Combines with Br_4. Lead salt sol. in ether. Absorbs oxygen rapidly from air	*Stearolic acid*, melts at 48°, and crystallises in long prisms. Combines with Br_2 to form dibromaleic acid, and with Br_4 to form tetrabromostearic acid	
$C_{19}H_{34}O_2$	Unknown	—	—		
$C_{20}H_{36}O_2$	Unknown	—	—	—	
$C_{21}H_{38}O_2$	Unknown	—	—	—	
$C_{22}H_{40}O_2$	—	—	—	*Behenolic acid*, melts at 57·5°, and crystallises in needles	

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[1] Elæomargaric acid forms rhombic plates which melt at 48°, absorb oxygen from the air and become resinous. On exposure to light the alcoholic solution deposits isomeric elæostearic acid, melting at 71. Both the solid isomers are converted into liquid elæolic acid when heated in an atmosphere of hydrogen to 180°.

D. *Higher Acids of the Linolenic Series*, $C_nH_{2n-6}O_2$.

Formula	Name of acid	Chief source or mode of occurrence	Other characters
$C_{18}H_{30}O_2$.	Linolenic acid .	As a glyceride in linseed and hemp oils	Liquid. Very oxidisable. Combines with Br_6. Forms linusic acid, melting at 203° when oxidised in alkaline solution. Pb salt sol. in ether
	Isolinolenic acid .	As a glyceride in linseed oil, together with some linolenic and linoleic acids	Resembles linolenic acid, but forms isolinusic acid, melting at 173-175° when oxidised in alkaline solution

E.—*Higher Acids of the Hydroxyoleic or Ricinoleic Series* $C_nH_{2n-2}O_3$, *or* $C_nH_{2n-3}(OH)O_2$.

Formula	Name of acid	Chief source or mode of occurrence	Other characters	Isomeric acids
$C_{18}H_{34}O_3$	Ricinoleic acid	As a glyceride in castor and curcas oils	Thick oily liquid, solidifying below 0°; sp.gr. ·951 at 15°. Miscible in all proportions with alcohol and ether. Combines with Br_2. Pb salt is sol. in ether; solidified by HNO_2; yields trihydroxystearic acid (ricinolic acid), melting at 140-142° when oxidised in alkaline solution. Yields *sebacic acid* when fused with KHO	*Ricinelaïdic acid*, produced by the action of HNO_2 on ricinoleic acid; melts at 50°, and crystallises from alcohol in silky glistening needles. Combines with Br_2. Pb salt melts at 100° and is soluble in ether
	Isoricinoleic acid	As a glyceride in castor oil, together with that of the isomer ricinoleic acid	Resembles ricinoleic acid	
	Rapic acid	As a glyceride in rape oil, together with that of erucic acid	Oily liquid. Zn salt is readily soluble in boiling ether (Zn erucate very sparingly soluble), and when crystallised from alcohol melts at 78°. Does not give sebacic acid when fused with KHO, but yields stearic and another crystalline acid instead. Not solidified by HNO_2. (See page 47.)	

All the fatty acids named in the foregoing tables are practically insoluble in water, but are mostly soluble in alcohol, ether, and fixed oils. In alcoholic solution they usually exhibit a more or less marked acid reaction, and both in solution and in the molten state decompose the carbonates of the alkali-metals. The resultant salts are commonly called 'soaps.' The fatty acids of the different series formulated in the foregoing tables present certain marked points of difference and general reactions of interest, of which the following are the chief:—

A. The higher acids of the *stearic series* are solid at the ordinary temperature. They are saturated bodies, and hence do not form additive compounds with bromine, and do not react with Hübl's iodine solution. They may be heated with caustic potash to a very considerable temperature (*e.g.* 300°C.) without change. They are equally unacted on by treatment with phosphorus and hydriodic acid. The lead salts of the acids of the stearic series are insoluble in ether, a fact which may be utilised to separate them as a class from all the acids of the following series.

B. The higher acids of the *oleic series* have lower melting-points than the acids of the stearic series containing the same number of carbon atoms. They form additive compounds with bromine of the formula $C_nH_{2n-2}Br_2O_2$, and react sharply with Hübl's reagent to form analogous compounds. When gradually heated with caustic potash to about 300° they yield potassium acetate, and the potassium salt of an acid of the stearic series containing a number of carbon atoms two less than the original acid of the oleic series employed:—

$$C_{18}H_{34}O_2 + 2KHO = C_2H_3KO_2 + C_{16}H_{31}KO_2 + H_2.$$

Heated rapidly with excess of alkali, certain of the acids of the oleic series yield *sebacic acid*, $C_{10}H_{18}O_4$, as a characteristic product. It forms brilliant needles, melting at 127°, and soluble in 1,000 parts of cold or 50 of boiling water. A remarkable reaction of oleic acid and its true homologues is the formation of an isomer of higher melting-point under the influence of nitrous acid. This reaction is common to their glycerides, and is also exhibited by ricinoleic acid and its glyceride, but not by the acids of classes *C* and *D*. When oxidised by permanganate in alkaline solution, oleic acid and its analogues yield acids of the dihydroxystearic series.

C. Linoleic acid and its *homologues* combine with either Br_2 or Br_4, and react with a larger proportion of Hübl's reagent than do the acids of the oleic series. They usually have a very low melting-point, are not visibly affected by nitrous acid, and form lead-salts soluble in ether. Linoleic acid absorbs oxygen rapidly from the air, and is oxidised by permanganate in alkaline solution to sativic acid (p. 47).

D. Linolenic acid and *isolinolenic acid* have only been recently proved to exist, and are now known chiefly through their products of oxidation in alkaline solution (*v.* p. 47). No homologues are known.

E. Ricinoleic acid combines with Br_2, does not oxidise in the air, is gradually solidified by nitrous acid, and forms a lead-salt soluble in ether. With permanganate in alkaline solution it yields a trihydroxystearic acid. With acetic anhydride, ricinoleic acid yields an acetyl derivative. No homologues of ricinoleic acid are known, and the isomers have been little studied.

The acids of the natural fixed oils, especially those of vegetable origin, are still imperfectly understood, and would well repay further investigation by the aid of modern methods of analysis. The following is a *résumé* of recent work in this direction.

The fatty acids of *rape oil* have been recently studied by Reimer and Will (B. 20, 2385), who state that besides a very small proportion of a solid acid which was identified as *behenic acid*, $C_{22}H_{44}O_2$, two liquid acids are present in about equal proportions. One of these, *erucic acid*, $C_{22}H_{42}O_2$, forms a zinc salt which is nearly insoluble in ether, which permits of its separation from *rapic acid*, $C_{18}H_{34}O_3$, the zinc salt of which is easily soluble in ether, and forms a crystalline mass, melting at 78°, from which the free acid may be obtained by heating with tartaric acid. Rapic acid is an isomer of ricinoleic acid. It cannot be solidified by cooling or treatment with nitrous acid, and when fused with potash yields, instead of sebacylic acid, stearic acid and a second crystallisable acid not yet fully examined. It evolves hydrogen when fused with caustic potash, and on dissolving the product in water and acidulating the solution a precipitate is formed from which two distinct crystallisable acids can be isolated by fractional crystallisation. For the preparation of behenic acid from rape oil 1,000 grams should be saponified, and the neutralised solution precipitated with 4 grams of zinc acetate. The precipitate is washed and decomposed by hydrochloric acid, and the product purified by crystallisation from alcohol. It forms shining silvery plates melting at 75°.

Benedict and Cantor (Z. 16) in criticising Reimer and Will's results, point out that the low acetyl number of rape oil (6·3) corresponds to only 3·8 p.c. of a hydroxyacid isomeric with that from castor oil. The high iodine-absorption of rape oil (100) as compared with the iodine-absorptions attributed by Reimer and Will to the acids isolated from it (erucic acid 75·2, rapic acid 85·2, behenic acid 0) renders it probable that there is a large proportion of an acid allied to linoleic acid present.

Goldschmidt has shown that the oil from *black mustard* seed contains the glycerides of erucic and behenic acids, and of another liquid acid which is probably identical with rapic acid.

The liquid portion of the fatty acids obtained by the saponification of *linseed oil* was till recently generally regarded as composed of linoleic acid, to which the formula $C_{16}H_{28}O_2$ was commonly attributed. A. H. Allen has shown that the figures on which this formula is based agree quite as well with $C_{18}H_{32}O_2$, and that as a fact the acid from linseed oil has a combining weight corresponding with the latter formula. To avoid confusion he has proposed to distinguish the C_{18} acid by the name homolinoleic acid, but this seems unnecessary since further researches have definitely proved the truth of Allen's conjecture. Thus Peters (M. 7, 552) has shown that when the acid, purified by conversion into its barium salt, is heated with phosphorus and hydriodic acid it yields stearic acid $C_{18}H_{36}O_2$, and not palmitic acid $C_{16}H_{32}O_2$, as would be the case if it contained 16 atoms of carbon. Similarly, Dieff and Reformatzky (B. 20, 1211) find that when oxidised by permanganate in alkaline solution linoleic acid is converted into a tetrahydroxystearic acid (sativic acid) $C_{18}H_{32}(OH)_4O_2$.[1] Hazura has arrived at the same conclusions on different grounds, and together with Grüssner has added much to the knowledge of the chemistry of the drying oils, and proves that in linseed oil two isomeric acids of the formula $C_{18}H_{30}O_2$ coexist with oleic and linoleic acids, though this conclusion is disputed by Reformatzky (J. pr. 41, 529). According to Hazura and Grüssner (M. 9, 180) when the fatty acids from *hemp-oil* are submitted in acetic acid solution to the action of bromine, brominated derivatives are formed which may be separated by crystallisation from alcohol. On heating the products with zinc and hydrochloric acid the bromine is eliminated and two unsaturated acids are obtained. Of these, linoleic acid $C_{18}H_{32}O_2$ absorbs I_4 from Hübl's solution, while the second product, called by the authors *linolenic acid* $C_{18}H_{30}O_2$ assimilates I_6. When these two acids are oxidised by potassium permanganate in alkaline solution they yield respectively sativic and linusic acid.

Sativic acid $C_{18}H_{32}O_2(OH)_4$ is insoluble in cold water and ether, soluble in 1,000 parts of boiling water, and is readily soluble in alcohol. From hot water it crystallises in long microscopic, silky needles or in pyramidal prisms, according to the purity and concentration of the solution. It melts at 173°. The potassium and sodium salts are soluble, the barium insoluble. Sativic acid, when treated with hydriodic acid, yields a brownish oily derivative which is converted into stearic acid by the action of nascent hydrogen. Hence sativic acid has probably the constitution of a tetrahydroxystearic acid.

Linusic acid $C_{18}H_{30}O_2(OH)_6$ is insoluble in cold water and ether, sparingly soluble in hot water and alcohol. It forms microscopic needles or rhombic plates (the opposite ends of which are often blunt) melting at 203°. The sodium and potassium salts are readily soluble, the barium easily in hot, but sparingly in cold water.

Isolinusic acid $C_{18}H_{36}O_8$, isomeric with the above, crystallises in small anhydrous prismatic needles, melting at 173-175°. It is insoluble in ether, benzene, chloroform, and carbon disulphide, sparingly soluble in cold water or cold alcohol, but readily in boiling water or alcohol. The potassium and sodium salts are readily soluble, and barium and calcium isolinusates are soluble in hot water.

From the researches outlined above, and similar experiments on ricinoleic and oleic acids, Hazura and Grüssner deduce the following law:—When oxidised by permanganate in alkaline solution, unsaturated fatty acids take up as many hydroxyl groups as there are free valencies, yielding saturated hydroxy-fatty acids containing the same number of carbon atoms in the molecule. The following is a tabular expression of the facts demonstrated by Hazura :—

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[1] Reformatzky (J. pr. 41, 529) has settled the formula of linoleic acid to be beyond dispute $C_{18}H_{32}O_2$. Ethyl linoleate was prepared by passing hydrochloric acid gas through an alcoholic solution of crude linoleic acid. The product was washed with water and unetherified fatty acid removed with 80 p.c. spirit. The purified and washed product was distilled under reduced pressure, the distillate saponified, the soap solution acidulated, and the free linoleic acid extracted by ether. The ethereal solution was evaporated, and the residue dried in a vacuous receiver over sulphuric acid, lime, and ferrous sulphate. The acid so prepared was a brownish, mobile, odourless oil, which had an iodine absorption of 180·3 (theory 181·43). By long-continued heating in a sealed tube with hydriodic acid it yielded $C_{18}H_{35}IO_2$, which on saponification yielded stearic acid.

Fatty acid		Oxidation product		
Name	Formula	Name	Formula	Melting pt.
Ricinoleic acid .	$C_{18}H_{33}O_2(OH)$	Trihydroxystearic acid	$C_{18}H_{23}O_2(OH)_3$	140–142°
Ricinisoleic acid .		Isotrihydroxystearic acid		110–111°
Oleic acid . .	$C_{18}H_{34}O_2$	Dihydroxystearic acid	$C_{18}H_{34}O_2(OH)_2$	
Elaïdic acid . .		Isodihydroxystearic acid		137°
Linoleic acid .	$C_{18}H_{32}O_2$	Tetrahydroxystearic acid (sativic acid)	$C_{18}H_{32}O_2(OH)_4$	173°
Linolenic acid .	$C_{18}H_{30}O_2$	Hexahydroxystearic acid (linusic acid)	$C_{18}H_{30}O_2(OH)_6$	203°
Isolinolenic acid .		Isolinusic acid		173–175°

Similarly, *brassic* or *erucic acid* $C_{28}H_{42}O_2$, melting at 32°–34°, yields dihydroxybehenic acid $C_{22}H_{42}O_2(OH)_2$, melting at 132°–133° ; while the isomer brassaïdic or erucaïdic acid $C_{22}H_{42}O_2$ obtained by the action of nitrous acid on erucic acid yields an isomeric dihydroxyacid, melting at 98°–99°C. Ricinelaidic acid yields by oxidation β-isotrihydroxystearic acid, melting at 114°–115°.

The best mode of operating in order to obtain the hydroxy-fatty acids is to treat 30 grams of the fatty acids in question with 30 c.c. of caustic potash solution of 1·25 sp.gr. The soap formed is dissolved in 2 litres of water, and treated gradually with 2 litres of a 1½ p.c. solution of potassium permanganate. The alkaline liquid is filtered and acidulated with sulphuric acid. The precipitated hydroxyacids (A) are collected, dried, and (converted in barium salts, the product being extracted with boiling water. The insoluble portion is decomposed by hydrochloric acid, and the liberated acids dried and) treated with cold ether. The solution contains *dihydroxystearic acid* (from oleic acid) and a small proportion of unoxidised acids. The portion insoluble in ether consists of *sativic acid* (from linoleic acid). The solution of the barium salts soluble in hot water is concentrated and acidulated. The acid set free consists chiefly of *linusic acid* (from linolenic acid), but is occasionally contaminated by small quantities of isolinusic acid, which may be removed by fractional crystallisation from alcohol. The acid liquid filtered from the insoluble hydroxyacids (A) is neutralised, concentrated to 300 c.c., and reacidified, when a precipitate of mixed *isolinusic acid* and *azaleic acid* $C_9H_{16}O_4$ is obtained. The precipitate is extracted with ether, in which the isolinusic acid is insoluble. The filtrate from the acidulated liquid yields to ether a small additional quantity of *azaleic acid*, and other lower fatty acids produced by the decomposition of linoleic acid.

Operating in this manner, Hazura and Grüssner conclude that the fatty acids from the vegetable oils have approximately the following composition :—

Liquid acids from	$C_{18}H_{34}O_2$ Oleic	$C_{18}H_{32}O_2$ Linoleic	$C_{18}H_{30}O_2$ Linolenic	$C_{18}H_{30}O_2$ Isolinolenic	Other acids
Linseed oil . .	present	15	15	65	—
Hemp oil . .	15	70	15	—	—
Nut oil . . .	7	80	13		—
Poppy oil . .	30	65	5		—
Cotton oil . .	40	60	—	—	
Castor oil . .	none	present	—	—	ricinoleic 1 ricinisoleic 2
Earthnut oil . .	present	present	—	—	hypogæic
Almond oil . .	present	present	—	—	—
Olive oil . .	93	7	—	—	—

These results show that linseed oil is peculiar in containing a very high percentage of acids of the formula $C_{18}H_{30}O_2$, a fact which explains its very high iodine-absorption, which is about 156, as against 135 for poppy oil. The uniform presence of linoleic acid in vegetable oils, and its absence from animal oleins (*e.g.*, lard oil) may be employed for the detection of the former class in mixtures. For this purpose the fatty acids are dissolved in caustic potash and treated with permanganate, as already described; but, in order to prevent the action going too far, with consequent loss of the characteristic product, sativic acid, the process of oxidation is allowed to continue for ten minutes only, when a rapid stream of sulphur dioxide is passed through the liquid till the solution becomes acid and all the oxide of manganese has redissolved. The sparingly soluble dihydroxystearic and sativic acids are filtered off, dried in the air, and washed with cold ether, which dissolves the former, together with any unoxidised acids, and leaves the sativic acid in a state of tolerable purity.

Recognition and Determination of Fatty Acids.

The methods available for the detection, and to some extent for the determination, of the higher fatty acids are for the most part based on the characters already described. In many cases it is unnecessary to effect an actual separation of the fatty acids of a mixture, it being sufficient to ascertain their joint amount, or to determine indirectly and approximately the proportion of the acids of different origins known to be present.

Methods not involving separation.—*a.* Free fatty acids can be volumetrically determined by the following process. Some methylated spirit is purified by redistillation with a little caustic soda, a little alcoholic solution of phenolphthaleïn added, and then dilute caustic soda added drop by drop till the liquid retains a faint pink colour after shaking, this preliminary treatment being intended to secure the absence of any trace of free acid. An accurately weighed quantity of the sample, varying from 5 grams of fatty acid to 50 grams of an ordinary oil, is then introduced into a flask or bottle furnished with a glass stopper. From 50 to 100 c.c. of the neutralised spirit is then added and raised to the boiling-point, either by immersing the bottle in hot water or by direct application of a flame. The contents are thoroughly agitated to effect as complete a solution of the fatty acids as possible. If the sample of oil be wholly free from acid, the pink colour of the spirit will remain unchanged, but otherwise it will have disappeared. In the latter case, a semi-normal solution of caustic soda (= 20·0 grams of NaHO per litre) is gradually added to the warm contents of the flask, which is thoroughly agitated after each addition. The addition is continued until a pink colouration is obtained, which persists after vigorous shaking. The reaction is as well defined, and the neutralisation-point as easy to perceive, as in the titration of mineral acids; but owing to the very high combining weights of the fatty acids, great care is necessary. Thus, 1 c.c. of normal caustic alkali used corresponds to 0·256 of free *palmitic*, 0·284 of free *stearic*, or 0·282 gram of free *oleic acid* in the quantity of the sample examined. For determining small proportions of free acid, it is desirable to employ decinormal alkali, while in the case of samples containing much free acid, the quantity taken for the assay should be correspondingly reduced. Glycerides, hydrocarbon-oils, and other neutral bodies do not interfere, but free mineral acids must first be removed by agitation with water, or determined by titration in alcoholic solution with methyl-orange as indicator, and resin acids must be separated or duly allowed for. In the case of a mixture of several fatty acids the result is best expressed in terms of the principal or most characteristic acid present, and in most cases such a mode of statement gives a close approximation to the true total of the free fatty acids present.

Conversely, when the substance under examination consists wholly of a mixture of fatty acids, titration with standard alkali suffices to ascertain the *mean combining weight* of the mixed acids. This is found by dividing the number of milligrammes of fatty acids employed for the titration by the number of cubic centimetres of normal alkali required for neutralisation. Thus if 5 grams of a mixture of free fatty acids has been found to require 37·80 c.c. of semi-normal alkali for its neutralisation, the mean combining weight of the acid will be 264·5, for:—

$$\frac{5000 \times 2}{37·8} = 264·5.$$

b. The method of Koettstorfer (page 24) may be regarded as a process for approximately ascertaining the mean combining weight of the fatty acids of an oil without actually isolating them. If the saponification-equivalent of the oil be multiplied by 0·95 the mean combining weight of the acids will be obtained with tolerable accuracy. The method is, of course, only applicable to oils yielding approximately 95 p.c. of fatty acids on saponification. With oils like shark and sperm oil, and the true waxes, the process is quite useless. On the other hand, in the case of the pure glycerides it is in some respects preferable to a titration of the previously isolated fatty acids, as there is less danger of alteration by oxidation or the loss of soluble fatty acids in the course of preparation.

c. The titration of a mixture of oleic acid with acids of the stearic series by means of Hübl's reagent allows the former constituent to be determined with considerable accuracy. As 282 parts of oleic acid, $C_{18}H_{34}O_2$, assimilate 254 parts of iodine, I_2, the iodine-absorption divided by 0·9 gives the percentage of *oleic acid* present. Linoleic acid and its homologues assimilate I_4, and hence their presence renders the determination of the oleic acid excessive, but the method is still applicable if the mode of calculation be modified accordingly. Oleic and linoleic acids have so very nearly the same molecular weight (282 : 280), that the latter may be regarded as absorbing twice as much iodine as the former, or 180 per cent. against 90. Hence, if 90 be subtracted from the observed iodine-absorption of the mixed acids, and the difference be divided by 0·9, the dividend will be the number of parts of linoleic acid in 100 parts of the mixture. If acids of the stearic series are also present, they must be separated or duly allowed for in making the calculation, which becomes hopelessly vitiated if linolenic acid be also present. If the percentages of stearic acid, oleic acid, and linoleic acid in a mixture of the three be represented respectively by the symbols s, o, and l, and iodine-absorption by A, the proportions of the liquid acids present will be found by the following equations:— s is known; $o = 200 - 1·11\ A$; and $l = 100 - o - s$.

Hübl's solution consists of an alcoholic solution of iodine containing mercuric chloride in a proportion not less than $HgCl_2$ to I_2. It is prepared by dissolving 25 grams of iodine in 500 c.c. of nearly absolute alcohol (free from fusel oil), and 30 grams of mercuric chloride in an equal measure of the same solvent. The latter solution is filtered, if necessary, and then added to the tincture of iodine. The mixed solution should be allowed to stand 12 hours before being used, as, owing to the impurities in the alcohol employed, it is liable to undergo considerable reduction in strength, and must in all cases be restandardised immediately before or after use. The strength is ascertained by titration with decinormal solution of sodium thiosulphate ($Na_2S_2O_3$), which in its turn is set by a solution of resublimed iodine in the usual way. The mercurial iodine solution reacts with ease at ordinary temperatures on either free unsaturated fatty acids or their glycerides, to form chloro-iodo-addition products, the total proportion of halogen assimilated being estimated in terms of iodine.

For the purpose of determining the iodine-absorption of an oil or fatty acid, from 0·2 to 1·0 gram according to its iodine-absorbing power should be weighed accurately and dissolved in 10 c.c. of chloroform. The solution is mixed in a stoppered flask with 20 c.c. of the standard solution of iodo-mercuric chloride, and if the liquid is not quite clear after agitation a further addition of chloroform is made. If the mixture becomes decolourised, or nearly so, after standing a short time, a further addition of 5 or 10 c.c. of iodine solution must be made. To ensure accurate results the excess of iodine must be very considerable, and hence the liquid ought still to be quite brown after standing for six hours. After remaining that time in darkness, from 10 to 15 c.c. of a 10 p.c. aqueous solution of potassium iodide should be added, or sufficient to redissolve any HgI_2 which may separate, and the whole diluted with about 150 c.c. of water. The free iodine, part of which exists in the aqueous and part in the chloroformic solution, is then determined by titration with standard thiosulphate, the contents of the flask being frequently and violently agitated, and starch solution being added just before the end of the reaction. A blank experiment with the same quantities of chloroform, iodine solution, &c., is made side by side with the actual test, so as to correct for any impurities in the reagents, and to ascertain the true strength of the iodine solution. The additional thiosulphate required in the experiment in which the oil was employed is then calculated into its equivalent of iodine, and this to units per cent. of the oil or fatty acids. In assaying free fatty acids by this process the use of chloroform is not essential, as, being soluble in alcohol, they are acted on by the iodine solution without its aid. Some operators allow a longer time (*e.g.* 12 hours) for the reaction to take place.

d. Much useful information respecting the fatty acids present in a mixture can be obtained by observing the melting and solidifying points, which are more or less characteristic of the fatty acids from different oils, as also are their specific gravities, iodine absorptions, and mean combining weights. The fatty acids should be prepared by saponifying the oil with alcoholic potash, taking great care that the reaction is complete. The alcohol is evaporated and the residual soap dissolved in hot water and decomposed by dilute sulphuric acid. The liquid having been well boiled, it is transferred to a flask and enough boiling water added to cause the layer of fatty acids to rise into the neck. They are removed with a pipette, and filtered in a hot water oven, through dry paper. There is no occasion to remove the trifling quantity of unsaponifiable matter present in most oils, but when shark, sperm, bottlenose oil, or any of the true waxes are under treatment, the alkaline solution of the soap must be repeatedly agitated with ether before acidifying the liquid.

Source of fatty acids	Melting-point °C.	Solidifying-point °C.	Specific gravity at 98°–100°	Mean combining weight	Iodine absorption
Olive oil	24–27	20–24	·843	279–286	90
Almond oil	14	5	—	278	—
Earthnut oil	28–33	24–31	·846	282	—
Rape oil	18–22	12–18	·844	307–321	105–106
Cottonseed oil	35–44	30–36	·848	275–289	115–116
Sesame oil	23–30	18–28	—	286–287	—
Nigerseed oil	25–27	—	—	—	—
Poppyseed oil	20–21	16–17	—	—	—
Linseed oil	24	17–18	·861	283	178–179
Hempseed oil	19	15	—	281	—
Walnut oil	20	16–17	—	274	—
Castor oil	13	2–3	·896	290–316	94
Palm oil	40–50	40–46	·837	263–273	53–54
Palm-nut oil	15	—	—	211	16–17
Cacao butter	48–52	49–51	—	—	—
Nutmeg butter	42–43	40	—	—	—
Shea butter	39–40	38	—	—	—
Cocoanut oil	24–25	20–21	·844	196–204	9–15
Japan wax	56	53	·848	252–261	—
Myrtle wax	47–48	46	·837	265	—
Lard oil	42–43	—	—	280	—
Lard	37–46	32–43	·837–·840	272–296	58–65
Compounded lard	39–43	—	·836–·839	—	—
Tallow	45–49	43–49	—	270–285	41–43
Beef suet	43	—	—	279	—
Margarine	42	40	—	—	—
Butter-fat (insoluble acids)	36–46	37–38	—	—	—
Sperm oil	13–14	—	—	281–294	88
Northern whale oil	—	—	·859	299	—

The preceding table shows the characters of the mixed (insoluble) fatty acids obtained by the saponification of various oils and fats. The variations in the melting and solidifying points are in great measure due to the different methods of observation adopted. The figures for the specific gravity at 98° to 100°C. are referred to water at 15°–16°C. taken as unity. The principal observers whose figures are quoted in the table are Allen, Archbutt, Bach, Bensemann, Dieterich, Dubois and Padé, Hübl, Thörner, Wiley, and Williams. Where the figures appeared to be highly exceptional they have been omitted as of doubtful accuracy. They have, in some instances, a considerable practical value. Thus, the high melting-point of the fatty acids obtained on saponification distinguishes cotton-seed oil from nearly all other liquid fixed oils of vegetable origin, and enables its presence to be inferred in admixture with other oils; the melting-point of the acids from cacao butter is remarkably constant, and is sometimes useful as a test of the purity of the fat; while the solidifying-point of the acids from palm oil affords a practical indication of the value of the sample to the candle manufacturer. The same remark applies to the fatty acids of tallow, for the proportion of oleic and solid fatty acids which a sample of tallow will yield can be deduced from the solidifying-point of the fatty acids. This is ascertained as follows. A test tube, about 5 inches in length by ⅔ inch in diameter, is fitted with a ring or collar of cork or india-rubber, by which it is fixed in the mouth of an empty bottle or flask. The melted substance is then poured into the (warmed) tube till it is about two-thirds filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, so that the bulb may be wholly immersed. When the fat commences to solidify at the bottom of the tube the thermometer must be attentively observed. The operator then stirs the contents of the tube slowly, by giving the thermometer a circular movement, first three times to the right and then thrice to the left. The first effect of the agitation is to cause the thermometer to fall slightly, but subsequently a sensible rise takes place, and the mercury remains stationary for at least two minutes. The temperature thus indicated is the solidifying-point of the substance, and the results obtained are remarkably constant. A rise of several degrees is often observed subsequently. In such cases both temperatures should be recorded.

The lowest permissible solidifying-point of the acids is often fixed at 44°C., corresponding to a mixture of oleic and solid fatty acids in equal proportions. The following table by F. Dalican shows the approximate yield of *solid fatty acids* ('stearic acid') from 100 parts of tallow or other fat. The corresponding *oleic acid* may be found by subtracting the percentage of solid acids from 95·00.

Solidifying-point °C.	Solid acids p.c.	Solidifying-point °C.	Solid acids p.c.
40·0	35·15	45·5	52·25
40·5	36·10	46·0	53·20
41·0	38·00	46·5	55·10
41·5	38·95	47·0	57·95
42·0	39·90	47·5	58·90
42·5	42·75	48·0	61·75
43·0	43·70	48·5	66·50
43·5	44·65	49·0	71·25
44·0	47·50	49·5	72·20
44·5	49·40	50·0	75·05
45·0	51·30		

(*e*) Another method of examining fatty acids, proposed by Benedikt and Ulzer, consists in preparing the acetyl derivative and then ascertaining, by Kœttstorfer's process, the amount of alkali required for its saponification. 50 grams of the fatty acid are boiled with 40 grams of acetic anhydride, under an inverted condenser, for two hours. The product is boiled with about 500 c.c. of water, washed till free from acid, dried and filtered. A known weight is then dissolved in alcohol and directly titrated with standard alkali as on p. 49. Another quantity is then saponified with a known quantity of KHO, as in Kœttstorfer's process, and the excess of alkali determined by titration with standard acid and phenolphthaleïn. Benedikt and Ulzer (Monatshefte, January 1887) give the following figures obtained by the process:—

Source of fatty acids	Original acids		Acetylated acids	
	KHO p.c. for neutralisation	Mean combining weight	Without saponifying. KHO p.c.	With saponification. KHO p.c.
Nut oil . . .	20·48	273·9	19·80	20·56
Cotton oil . . .	19·98	280·8	19·57	21·23
Croton oil . . .	20·10	279·1	19·57	20·42
Hemp oil . . .	19·94	281·3	19·68	20·43
Almond oil . .	20·16	278·3	19·65	20·23
Olive oil . . .	19·71	284·6	19·73	20·20
Castor oil . . .	17·74	316·2	14·28	29·62

The process of Benedikt and Ulzer is based on the assumption that only hydroxylated fatty acids (*e.g.* ricinoleic acid) form acetylated derivatives when heated with acetic anhydride, the others remaining unaltered, so that in the latter case the proportions of alkali required will be approximately the same before and after acetylisation. J. Lewkowitsch (C. N. vol. 61, 238, 286; S. C. I. 9, 842) has published results which appear to prove conclusively that the reaction with acetic anhydride is not so simple, or the figures so reliable, as was supposed. Acetic anhydride appears to act on stearic acid to form stearic anhydride and acetic acid. After washing with water the stearic anhydride is but slowly hydrolysed by aqueous potash, but if dissolved in alcohol and titrated with caustic alkali it undergoes immediate hydrolysis, and hence neutralises the alkali, just like stearic acid. This fact prevented Benedikt and Ulzer from discovering the change. The other higher fatty acids behave similarly. Lewkowitsch points out that, in the light of his researches, the presence of hydroxylated fatty acids (*e.g.* ricinoleic acid) cannot be safely inferred unless the difference in the amount of alkali required for neutralising the fatty acids before and after treatment with acetic anhydride exceeds the limits of possible experimental error. He suggests that where the presence of hydroxylated acids is proved the best method of estimating the amount will be to saponify the acetylated acids with alcoholic potash, boil off the alcohol, acidulate with sulphuric acid, distil off the acetic acid, and ascertain its amount by titration of the distillate.

Methods of analysing fatty acids involving separation.—The actual separation of mixed fatty acids is often a problem of extreme difficulty, which indeed cannot in all cases be satisfactorily solved in the present condition of chemistry. The principles which have been applied to the fatty acids enumerated in the tables on page 43 *et seq.* include the following:—

1. The mixed free fatty acids are well washed by agitation with hot water, when those containing 10 atoms or fewer of carbon are dissolved. This process is applied to the analysis of the fatty acids from butter.

2. The mixed free fatty acids obtained by treating their soaps with a moderate excess of dilute sulphuric acid (sufficient to convert the alkali into $MHSO_4$) are distilled with water, either with or without the aid of a current of open steam. This method allows a more or less complete separation of the homologues up to lauric acid from the higher members of the stearic series.

3. The acids are converted into barium salts, and the precipitate treated with water or alcohol. The barium salts of lower members up to capric acid can be dissolved out by boiling water.

4. The acids are converted into lead salts, which are then treated with ether or alcohol. An application of this principle enables the higher acids of the stearic series to be separated from the fatty acids of the remaining series.

5. The alcoholic solution of the acids is precipitated by magnesium acetate. By operating fractionally some useful and difficult separations can be effected.

6. Fractional distillation, fractional fusion and pressure, and fractional solution in or crystallisation from alcohol or other solvents, are other processes employed for the separation of the fatty acids.

No precise method of *separating* oleic acid and its homologues from linoleic acid has hitherto been devised. Possibly one might be based on the conversion of the acids of the oleic series into isomers of higher melting-point and modified properties by means of nitrous acid. Methods 1, 2, and 3 have been already sufficiently described, and those under 6 do not require further notice. Methods 4 and 5, however, are described below.

The higher homologues of the stearic series of fatty acids being solid at ordinary temperatures, while the fatty acids of other series (*e.g.* oleic, linoleic, ricinoleic) are liquid, a more or less complete separation can be effected by subjecting the mixture to filtration or pressure. The latter plan is employed with considerable success on a large scale. Crystallisation from hot alcohol also serves to free the solid fatty acids from those fluid at ordinary temperatures, but neither plan allows of the latter being obtained even moderately free from admixed solid acids, and such methods are quite useless for quantitative work.

A general method by which stearic acid and its homologues can be separated from oleic and other liquid fatty acids is based on the insolubility of the lead salts of the acids of the stearic series in ether, and the solubility of the corresponding compounds of other fatty acids in the same menstruum. The best method of operating is probably that recommended by J. Muter (An. 14, 63). Three grams of the fat should be treated in a flask furnished with a long tube with 50 c.c. of alcohol and fragment of caustic potash. The contents of the flask are heated to boiling till saponification is complete, when a drop of phenolphthaleïn solution is added, and then acetic acid till the liquid is slightly acid. An alcoholic solution of caustic potash is then added drop by drop till a faint permanent pink tint is obtained, when the liquid is slowly poured, with constant stirring, into a basin containing a solution of 3 grams of neutral lead acetate in 200 c.c. of boiling water. The whole is allowed to cool slowly, stirring well to induce agglomeration of the precipitate, and the clear liquid is then poured off. The precipitate is well washed by decantation with boiling water, and then transferred to a stoppered bottle, where it is treated with 120 c.c. of ether and allowed to remain twelve hours, when any oleate, hypogæate, linoleate, or ricinoleate of lead will have been dissolved by the ether, leaving laurate, myristate, palmitate, arachidate, &c., insoluble. Lead eruceate is very sparingly soluble in cold ether, but readily in hot. (Petroleum ether might probably be substituted without detriment to the accuracy of the separation, but if rectified spirit be employed instead of ether, more or less arachidate, myristate, and laurate of lead may pass into solution, in addition to the lead salts soluble in ether.) The contents of the bottle are then filtered through a covered filter into a wide graduated tube or burette furnished with a stopper at the top, a glass tap at the bottom, and a second glass tap about 50 c.c. from the bottom. 40 c.c. of dilute hydrochloric acid (1 : 4) is then added, and the burette shaken till the clearing of the ethereal liquid shows that the decomposition of the lead soaps is complete. The aqueous liquid, containing lead chloride and excess of hydrochloric acid, is run off through the bottom tap, water added, and agitated with the ether, and the process of washing by agitation repeated till the removal of the acid is complete. Water is then added to the zero mark, and then sufficient ether to bring the ethereal solution to a definite volume (*e.g.* 200 c.c.). An aliquot portion of this (*e.g.* 50 c.c.) is then removed through the side-tap and the residual fatty acid weighed after evaporation of the ether, preferably conducted in a current of coal gas or carbon dioxide. Another aliquot portion of the ethereal solution should be distilled to a small bulk (avoiding complete evaporation of the ether), alcohol added, and the solution titrated with decinormal caustic alkali and phenolphthaleïn, when the fatty acids can be calculated from the result, or their mean combining weight deduced therefrom. A third aliquot part of the ethereal solution should be evaporated at about 60°C. in a flask traversed by a rapid current of dry carbon dioxide. When every trace of ether is removed, 50 c.c. of Hübl's iodine solution should be added, the stopper inserted and the liquid kept in absolute darkness for twelve hours, after which excess of potassium iodide solution is added, and 250 c.c. of water, when the excess of iodine is ascertained by titration with decinormal sodium thiosulphate in the usual way. From the result, the iodine equivalent of the fatty acids can be calculated and an opinion formed respecting the proportions of oleic, linoleic, and other unsaturated acids present.

In a more recent paper (An. 15, 48) Muter and De Koninck give the iodine absorptions of the liquid acids prepared by the above process from various sources. Thus the oleic acid from tallow has an iodine-absorption of 90; from lard 93; and cottonseed oil 135. Asboth has obtained practically identical figures, and expresses a favourable opinion of the process (Chem. Zeit. 14, 418).

To estimate the stearic and homologous acids, the lead soaps insoluble in ether should be detached from the filter and heated with diluted hydrochloric acid, the liberated fatty acids being allowed to solidify, and then directly removed and weighed; or dissolved in ether-alcohol, and the solution evaporated to dryness. The product may contain arachidic, stearic, palmitic, myristic, and lauric acids, besides the less commonly occurring members of the same series. The separation of these homologues is extremely difficult, and a quantitative separation of several immediate homologues occurring together in a mixture is especially so. The solubility of the homologues in alcohol rapidly diminishes with an increase of the number of carbon-atoms in the acid, and advantage may be taken of the very limited solubility of *arachidic acid* to effect its separation from lower homologues; 2 grams of the solid fatty acids to be tested should be dissolved in 50 c.c. of hot alcohol (sp.gr. ·830). On cooling, abundant crystals will be immediately formed if arachidic acid be present. They should be filtered off, washed twice with 10 c.c. of cold rectified spirit, and then with spirit of ·890 sp.gr., in which they are completely insoluble. A correction of ·0025 gram for each 10 c.c. of rectified spirit used for the crystallisation and washing, if the manipulation be conducted at 15°C., or ·0045 gram for 10 c.c. if at 20°C., will enable an approximate quantitative result to be obtained under favourable conditions. If a drop of an alcoholic solution of mixed stearic and arachidic acids be allowed to evaporate spontaneously, the arachidic acid crystallises out first in short single needles, which soon unite into beautiful ramified masses of characteristic shape, and which cannot be confounded with the more rounded ice-like crystals of stearic acid.

Fractional precipitation by alcoholic solutions of the acetates of lead, barium, and magnesium have been employed for the separation of the higher solid fatty acids, but no reagent has been found which will allow of a complete precipitation of certain of the homologues while leaving others wholly in solution. The most satisfactory method for the purpose in question is that of Heintz (J. pr. 66, 1), based on fractional precipitation of the alcoholic solution of the acids with magnesium acetate. This salt precipitates acids of the stearic series more easily than it does oleic acid and its homologues, and of the homologues of the stearic series those of the highest molecular weights are thrown down first. In practice, 40 grams of the mixed fatty acids should be dissolved in such a proportion of hot alcohol that nothing will separate on cooling, even at 0°, and the hot liquid treated with a boiling alcoholic solution of 1·5 grams of magnesium acetate. The liquid is filtered when cold, and the filtrate heated and treated again with alcoholic magnesium acetate, the second precipitate being separated, and the treatment repeated as long as anything is thrown down. To induce precipitation of the lower homologues the liquid must be rendered alkaline with strong ammonia before adding the precipitant, and not filtered for twenty-four hours. The first fractions contain magnesium stearate and any higher homologues, the succeeding portions will consist chiefly of magnesium palmitate, and the last will probably contain myristate; but a portion of the myristic acid, the whole or nearly the whole of the lauric acid, and any oleic acid which may be present will remain in solution, and may be precipitated by lead acetate after neutralising the liquid with acetic acid. After washing the precipitate with cold dilute alcohol, any lead oleate can be dissolved out by treatment with ether. The purified lead precipitate and various magnesian precipitates should be washed with cold alcohol, pressed, and decomposed by hot dilute hydrochloric acid, and washed repeatedly with hot water.

The several fractions of fatty acids thus obtained, after being weighed if desired, may then be titrated in alcoholic solution with standard alkali and phenolphthaleïn as described on page 49.

As a rule, if the mixed fatty acids be divided into a sufficient number of fractions, by precipitation with magnesium acetate, each fraction will contain only two homologues, in which case the result of the titration not only indicates the nature of the homologues present, but in many cases allows of their relative proportions being calculated. Thus, if, in the course of a systematic fractional precipitation as magnesium salts, a fraction of fatty acids be obtained having a mean combining weight of 264·5, it will almost certainly consist essentially of a mixture of stearic and palmitic acids, the former of which has the molecular weight 284 and the latter 256, the difference being 28. Hence, every 1 p.c. of stearic acid in the mixture will raise the combining weight ·28, or for every unit above 256 found for the combining weight of the fraction 3·57 of stearic acid should be calculated. Thus a fraction having the mean combining weight 264·5 will contain 69·7 of palmitic and 30·3 p.c. of stearic acid, for

$$\begin{array}{rr} 264{\cdot}5 & \\ -256{\cdot}0 & {\cdot}100{\cdot}000 \\ \hline 8{\cdot}5 \times 3{\cdot}57 = & 30{\cdot}345 \\ & \overline{69{\cdot}655} \end{array}$$

As with all indirect methods of the kind, the results obtained are fairly satisfactory when both constituents are present in considerable proportion, but are of little value for mixtures in which one constituent very largely predominates.

The titration having been completed, the alcohol may be boiled off and the fatty acids again liberated and subjected to renewed fractional precipitation or crystallisation from alcohol. The products so obtained can be again titrated, and thus the progress of the isolation and purification of the different fatty acids checked in a very simple and satisfactory manner.

Valuable information respecting the composition of the various fractions obtained by the precipitation as magnesium salts is derived from the determination of the melting-points of the fatty acids, but unfortunately, the melting-point of a mixture of two or more homologous fatty acids is not the mean of the melting-points of the constituent acids. Still, the melting-points of various mixtures of solid fatty acids have been very carefully determined by Heintz, who has also noticed that the mixtures, on solidifying, crystallise in more or less characteristic forms, or remain amorphous, according to the proportions in which the constituents are present.

Heintz also noticed that the addition of a third acid, even of higher melting-point, to a mixture of two homologous acids caused a lowering of the melting-point.

The determination of the melting-point of a mixture of two or more fatty acids taken alone is evidently incapable of giving very definite information; but if the observation be associated with other data very useful inferences can be drawn. Thus the following mixtures of homologous fatty acids melt at nearly the same temperature, but may be distinguished by determining their combining weights, by titrating them in alcoholic solution with standard caustic alkali and phenolphthaleïn :—

Nature of mixed fatty acids				Melting-point	Mean combining weight
Lauric	Myristic	Palmitic	Stearic		
30	70	—	—	46·7	219·6
50	—	50	-	47·0	228·0
	70	30	—	46·2	239·4
—	50	21	29	43·5	250·0

Resin is best separated from fatty acids by dissolving 4 grams of a mixture of the two (previously separated from glycerides and hydrocarbons) in alcohol, adding phenolphthaleïn, and then caustic soda till the pink tint is just permanent. The solution is then evaporated to dryness at 100° with addition of some clean sand, which is thoroughly incorporated with the soap before solidification occurs. The residue is finely powdered and thoroughly dried in the water oven, and is then transferred while still warm to a stoppered graduated tube, having a side tap about one-third of the way up. 150 c.c. of ether and 30 c.c. of alcohol, both rendered as dry as possible by being kept over an excess of recently ignited potassium carbonate, are then added, the tube closed, and the contents agitated at intervals for some hours and then allowed to settle thoroughly. The solvent dissolves the resin soap with facility, but leaves the sodium palmitate and stearate unchanged, while sodium oleate is but slightly soluble (1 in 935). A known measure of the liquid is then removed by the tap, when the dissolved resin may be determined by agitating the ethereal liquid with water and dilute sulphuric acid, separating the ethereal layer and evaporating it to dryness. The result is seriously vitiated in presence of oleic and other liquid fatty acids, and it is better in all cases to transfer a known measure of the ether-alcohol solution of the resin soap to another similar tube, and there agitate it thoroughly with about 1½ grams of silver nitrate in the form of impalpable powder. The agitation is continued for ten minutes, or until the precipitated silver oleate coagulates and leaves the liquid clear. An aliquot part of the ethereal liquid is then run off into a tapped separator in which it is shaken with a small additional quantity of silver nitrate, to ensure that the whole of the fatty acids have been precipitated. If any flocculent precipitate be produced, the liquid should be returned to the cylinder, shaken with more silver nitrate, and a known volume again removed by means of the tap. The measured ethereal liquid in the separator is then vigorously shaken with about 10 c.c. of hydrochloric acid and 20 of water, whereby silver chloride is precipitated and the liberated resin acids remain dissolved in the ethereal layer. This is separated from the aqueous liquid, evaporated to dryness, and the residue weighed. Gladding, who devised the process (Am. [3] 1206), directs that the weight obtained shall be corrected by subtracting 2·35 milligrammes for each 10 c.c. of ethereal liquid removed by the tap (=0·0352 gram for 150 c.c.), this being an allowance for the slight solubility of silver oleate in the ethereal liquid.

This correction was based on experiments made by the silver process only, not preceded by a treatment of sodium salts by ether-alcohol as devised by Barfoed and recommended above. Wright and Thompson (S.C.I. [4] 630) find that Gladding's correction is excessive when either stearic or oleic acid is alone present (with resin acids) though approximately accurate for mixtures of the two. They further find that the correction is insufficient in the case of fatty acids of other kinds, and especially with the acids from castor oil. The following results were obtained by them :—

—	Milligrammes of fatty acids in 10 c.c. of solvent		
	Max.	Min.	Average
Pure oleic acid . .	1·5	0·9	1·20
Pure stearic acid . .	1·6	0·8	1·16
Mixed stearic and oleic acids	2·2	1·8	1·91
Acids from cottonseed oil	3·4	2·0	2·69
Acids from castor oil .	6·2	4·9	5·39
Acids from cocoanut oil .	2·3	1·3	1·80
Acids from linseed oil (Allen) . . .	—	—	2·31

When carefully worked, and especially when preceded by Barfoed's treatment of the sodium soaps with ether-alcohol, Gladding's process gives very satisfactory results, the resin isolated being often brittle and possessed of all the characters of colophony.

Another process, also based on the different behaviour of the silver salts of fatty and resin acids with ether, has been devised by Hübl and Stadler, and is stated by Schnaible to give good results. 0·5 to 1·0 gram of the mixed acids is dissolved in 20 c.c. of alcohol, and the solution rendered exactly neutral to phenolphthaleïn. It is then diluted with water to 200 c.c., and precipitated with silver nitrate. The precipitate (which must be protected from bright light) is filtered off, washed, dried at 100°, and extracted with ether. The ethereal solution, which should be yellow or light brown, but not dark brown, is shaken with hydrochloric acid, separated, washed with water, and evaporated. The weight of resin acids obtained should be multiplied by the factor 0·9732 to obtain the weight of anhydrous resin. A. H. A.

OILSTONE. A fine-grained hone-stone used with oil, for sharpening edged tools. The most celebrated is the Turkey oilstone, an extremely hard and compact material, obtained in the interior of Asia Minor, and exported from Smyrna. Two varieties are recognised, the white and the black, the latter being slightly the harder. In this country the Charley Forest stone has obtained great repute as an oilstone for whetting tools and penknives. It is a fine-grained, siliceous, slaty rock, worked at Whittle Hill in Charnwood Forest, Leicestershire. The Welsh oilstone is a somewhat similar material, from near Llyn Idwal in North Wales; while the Devonshire oilstones are obtained from the neighbourhood of Tavistock. Several kinds of oilstone are worked in the United States. The Arkansas stone is a compact or fine-grained rock of bluish-white colour, used for delicate instruments, like those of surgeons and watchmakers. Somewhat similar, but more abundant, is the Washita oilstone, a white opaque stone used chiefly by carpenters. The Labrador oilstone, of New York, is a fine-grained slate-coloured sandstone.

In preparing oilstones for use, the rough pieces are cut into regular shapes on the lapidary's wheel, fed with diamond powder, and are rubbed smooth with sand or emery on an iron plate. The slab of stone is in some cases cemented to a wooden base, by means of putty. Some of the stones are used not only for sharpening tools, but for finishing turned and planed surfaces of metal work. Oilstone powder is also employed for grinding the brass fittings of mathematical instruments (*v.* R. Knight, Trans. Soc. Arts, 50, 233; C. Holtzapffel, Turning, vol. 3, 1081; and G. M. Turner, Min. Res. U. S. for 1885, 433; and for 1886, 589; *v.* also WHETSTONES). F. W. R.

OKENITE *v.* CALCIUM.

OLEFIANT GAS *v.* ETHYLENE.

OLEFINES. Hydrocarbons of the C_nH_{2n} series homologous with ethylene.

OLEIC ACIDS. This term is applied to the acrylic or oleic series of acids, or more particularly to the higher members of that series. Such higher members, the only ones considered here, are characterised by the solubility of their lead salts in ether, in which respect they differ from stearic, palmitic, and other acids with which they occur, and by their conversion, under the action of nitrous acid, into isomerides of higher melting-point. They cannot be distilled unchanged except *in vacuo* or with the aid of steam.

Hypogæic acid $C_{16}H_{30}O_2$ occurs with palmitic and arachidic acids in earthnut oil, and may be obtained by methods similar to those used in the case of oleic acid. It forms colourless needles, melting at 33° and readily soluble in alcohol. Under the action of nitrous acid, it forms an isomeride, *gæidinic acid*, which melts at 39°. *Physetoleic acid*, another isomeride melting at 30°, occurs in spermaceti oil.

Doeglic acid $C_{19}H_{36}O_2$ and **Erucic** or **Brassic acid** $C_{22}H_{42}O_2$, occur respectively in the doegling train-oil obtained from the bottle-nosed whale, and in mustard and rape-seed oils (*v.* page 20).

Oleic acid $C_{18}H_{34}O_2$, the only commercially important member of the series, occurs as the glyceride, triolein $C_3H_5(C_{18}H_{33}O_2)_3$, in most liquid and solid fats, such as non-drying oils, almond, olive, and cod-liver oils, and in lard, tallow, palm oil, butter, &c. It is obtained in large quantities as a by-product in the separation of stearin in candle-making.

Preparation.—The pure acid may be prepared by saponifying almond or olive oil with alkali, dissolving the soap thus obtained in water, and decomposing it by addition of dilute hydrochloric or sulphuric acid. The separated oleic acid is digested on the water-bath with 1 part of finely-powdered litharge for every 20 parts of oil used. All the palmitic and stearic acid, and much of the oleic acid, is thus precipitated as a lead salt. Excess of litharge is avoided, to prevent the production of a basic oleate, which is difficult to treat.

The lead soap thus obtained is heated with two volumes of ether which dissolves the lead oleate only, and the decanted ether is shaken up with dilute hydrochloric acid, which is added until the aqueous liquor remains strongly acid. The ethereal solution of the free acid is then separated from the aqueous solution of lead chloride and is washed with water and freed from ether by evaporation at a low temperature.

The oil may be saponified directly by boiling with litharge, as recommended by Wolff, who also employs petroleum spirit instead of ether.

Colouring matter and oxidation products may be removed by pressing between filter-paper, fusing, cooling, and re-pressing.

To prepare perfectly pure oleic acid, the acid is dissolved in ammonia and treated with barium chloride. The precipitate is recrystallised from alcohol and decomposed by tartaric or other acid.

For the commercial production of oleic acid three principal processes are in use. (1) The oil, or the original fat, is decomposed by lime or other base, which may be used in excess at the ordinary or slightly elevated pressures, or in smaller quantities at higher pressures. The lime salt is finally decomposed by treatment with dilute sulphuric acid. (2) The oil or fat is treated with superheated steam at elevated pressures. (3) Boiling water at the normal pressure is used, the fat being first treated with sufficient sulphuric acid to destroy the envelopes of the fat cells without materially discolouring the fat. The treatment may be effected as follows: 50 kilos. of the muddy acid liquor from a previous operation is poured into a steam-heated copper vessel together with 1,000 kilos. of chopped fat, added in four charges, with 5 kilos. of sulphuric acid (1·84 sp.gr.) and 150 litres of water. After heating for about 2½ hours, to 105° to 110°, the acid has so decomposed the skin of the cells that the fat easily runs out. The fat is run off and mixed with a solution of alum containing 1½ to 2 kilos. in 20 litres, and the clear fat is removed after settling for several hours.

In another process, the fat is first treated with concentrated sulphuric acid to decompose the membranes, and is then washed and distilled with superheated steam at about 300°.

Evrard of Douai dissolves the membranes by treating the fat with a dilute alkaline lye, preferably a soda lye of 1·25 sp.gr. The mixture is heated by a steam jet and is covered by a perforated plate, which sinks as the separated fat rises through it.

In De Milly's largely-used 'autoclave' process, one ton of a mixture of tallow and palm oil, or of other neutral fat, is heated with 2 p.c. of lime and one-third its volume of water at a pressure of eight atmospheres for four hours. The lime soap thus obtained is decomposed as usual with dilute sulphuric acid.

One ton of good tallow yields about half its weight of oleic acid.

An impure oleic acid, known as 'olein' or 'wool oil,' and employed for oiling wool and for making lubricants and soaps, is prepared from the 'Yorkshire grease' obtained from the soap used in cleaning, milling, and oiling fibres, yarns, and cloth.

The grease is first treated with hydrochloric or sulphuric acid, and the separated oil is distilled with superheated steam. The principal part of the product is a thin, limpid, pale-yellow oil which cools to a grease known as 'first distilled grease.' This is redistilled, or may be compressed to obtain oleic and stearic acids. It yields about 66 p.c. of the former (*v.* Hurst, S. C. I. 1889, 91).

The fact that oleic acid splits up when fused with potash into acetic and palmitic acids has been proposed by Varrentrapp and applied by St. Cyr Radisson for the preparation of the latter acid on the manufacturing scale (Eng. Pat. 1869, No. 1,782; Lant Carpenter, S. C. I. 1883, 98, and 1884, 200; and Spon's Encyc. of Manufactures &c., p. 584).

A mixture of 1½ tons of oleic acid and 2½ tons of caustic potash lye of 43°B. is heated in a cast-iron cylinder, 5 feet high and 12 feet in diameter, by a fire placed some distance below the bottom of the vessel. When steam ceases to escape, a man-hole in the cylinder is closed, so that the gases afterwards evolved may pass through a condensing tower to a gas-holder.

The mass, which is mixed by a mechanical agitator, gradually rises in temperature to about 330°, at which point the evolved gases acquire a characteristic odour which indicates the necessity to stop the action lest destructive distillation commence. The action is then suddenly arrested by the introduction of steam and water by an injector, while a door in the cylinder is opened so that the mass falls into a tank, in which it is mixed with water and heated by steam.

After subsidence, the neutral potassium palmitate, which forms a layer above the potash lye, is removed, decomposed with sulphuric acid, and washed free from potassium sulphate. The clear, chocolate-coloured acid gives, when distilled, a fine white product excellent for candle-making, and capable, when mixed with stearic acid, of rendering the same less crystalline, so that the candles prepared from a suitable mixture have a highly-prized semi-transparency.

The hydrocarbons collected in the condensing towers are good illuminants.

The palmitic acid obtained is said to amount to 90 p.c. of the weight of the original oleic acid. This large product is doubtless due to the presence of palmitic and other acids in the oleic acid employed.

The reaction cannot be performed in the ordinary manner when soda lye is employed, on account of the higher temperature required, and the difficulty of preventing local superheating. The addition, however, of paraffin renders the whole fluid and overcomes these difficulties.

It is stated that all fatty bodies except mare's grease and suint fat may be worked up by this process.

Among other processes which have been proposed, though not yet employed on the manufacturing scale, for converting oleic acid into the more useful solid products, may be mentioned the preparation of elaïdic acid, described under the properties of oleic acid; the preparation of stearic acid by heating oleic acid with a small quantity of a halogen as proposed by Wilde and Reychler; and the treatment of oleic acid with zinc chloride as proposed by Schmidt.

The latter process, which has been examined by Benedikt (Monatsh. 1890 [2] 71), consists in digesting 10 parts of oleic acid with 1 part of zinc chloride at 180° to 185° until the zinc chloride has dissolved and a drop of the mixture when boiled with hydrochloric acid solidifies on cooling. Dilute hydrochloric acid is then added, and the mixture is heated by steam until the washings no longer contain zinc, after which the product is distilled under somewhat reduced pressure. The solid matter separated by pressure from the distillate contains about 75 p.c. of stearo-lactone and about 15 p.c. of an acid identical with the iso-oleic acid described by Saytzeff, as mentioned below.

Properties.—Pure oleic acid is a thin, colourless, tasteless oil of sp. gr. 0·897 at 19° and 0·876 at 100°. It distils in superheated steam at 250°, but, if distilled alone, is split up into acetic, caprylic, caproic, and sebacic acids, with evolution of carbon dioxide and hydrocarbons. Oleic acid solidifies at about 4° to a white crystalline mass. From an alcoholic solution it separates out in dazzling needles, which melt at 14°.

Oleic acid is insoluble in water, but dissolves readily in alcohol, ether, carbon bisulphide, chloroform, and hydrocarbons, and in neutral fats and essential oils. The alcoholic solution of the pure acid is stated to be neutral, but the solution of the commercial product is decidedly acid. Pure oleic acid is almost unaltered in air, but the commercial acid gradually absorbs oxygen and acquires a lower melting-point.

Oleic acid dissolves in strong sulphuric acid with production of a colourless sulphonic acid known as *sulpholeic acid.* The sodium, ammonium, or potassium salt of this acid is employed in the dyeing of cotton goods by alizarin, under the name of 'alizarin oil,' 'turkey-red oil,' 'red oil' or 'oleine,' but is not equal to the sulphoricinoleate prepared from castor oil for this purpose. It is also used as a 'prepare' for steam colours in calico-printing.

Sulpholeic acid may be prepared by gradually mixing almond or other fixed oil with 30 to 40 parts of concentrated sulphuric acid, cooling with ice if necessary, to prevent rise of temperature above 50°. The mixture is left for from 6 to 12 hours, after which the acid and glycerin are removed, and the residue is agitated with 100 parts of water and decanted and neutralised with alkali or carbonate. Pure sulpholeic acid may be obtained by cautious addition of sulphuric acid to the alkaline salt and agitation with ether. On decanting and evaporating the ethereal solution, the free acid, which is insoluble in water, is obtained (*v.* Pharm. Rundschau, 1885, 154, and U. S. Dispensatory, 1889, 1025).

Free sulpholeic acid and sulpholeates, especially the sodium salt when pure and concentrated, mix readily and completely with various organic compounds, such as essential oils and hydrocarbons and their halogen derivatives, the mixtures giving emulsions or even clear liquids with water. Sulphur, iodoform, solid hydrocarbons, camphor, &c., are also dissolved by this acid and its salts.

Oleic acid yields stearic acid when heated with amorphous phosphorus and fuming hydriodic acid at 200° to 210° in a sealed tube.

When nitrogen trioxide is passed in small quantity into well-cooled oleic acid the mass gradually thickens, and in about an hour solidifies. The product, when washed and crystallised from alcohol, gives large pearly plates melting at 44°–45°, and having a strong acid reaction.

This body is *elaïdic acid*, an isomeride of oleic acid, and has been proposed, on account of its high melting-point, for use in candle-making. Only a portion of the oleic acid is thus isomerised. Saytzeff (J. Russ. Chem. Soc. 1886, 328, and J. pr. 37, 269) describes another solid isomeride, which he calls *iso-oleic acid.* It solidifies at 44°–45°, and is obtained with ordinary oleic acid by distillation under reduced pressure of hydrostearic acid, which is prepared by the action of sulphuric acid and water on oleic acid.

Commercial oleic acid, frequently known as 'red oil' and 'oleine,' varies from a clear liquid to a paste, and from a pale-yellow to a dark-brown colour. It usually contains triolein, which may be present in considerable quantities when saponification has been imperfect. A small proportion of hydrocarbons is always present. When the acid is adulterated with mineral or shale oil this proportion becomes considerable.

Linoleic acid is frequently found in oleic acid, either due to adulteration with linseed or other oil, or to the addition of linseed oil to stearin, to facilitate the removal of olein by pressure (*v.* Granval and Valser, J. Pharm. Chem. 1889, 232, and Hazura, Zeits. f. angew. Chem. 1889, 283).

Oleates. Oleic acid forms a number of well-defined salts, many of which are now employed medicinally in the form of solutions in excess of free oleic acid, in place of the less energetic ointments prepared from fats. There is a strong tendency to the formation of basic and acid salts. Oleates are best prepared from the sodium salt by double decomposition, but for medicinal use are usually made by dissolving the freshly-precipitated oxide or other agent in the acid.

Only the alkaline salts are soluble in water. Most of the remainder dissolve in alcohol, ether, carbon bisulphide, and petroleum spirit. Calcium, magnesium, and iron oleates are also soluble in glycerin.

Sodium oleate $C_{18}H_{33}O_2Na$ forms a principal constituent of hard soap. It may be prepared by neutralising an alcoholic solution of the acid with soda and evaporating off the alcohol. This salt, which crystallises out from absolute alcohol but not from water, dissolves in ten or twelve parts of water. It gelatinises in air without deliquescence.

Potassium oleate $C_{18}H_{33}O_2K$ is a principal constituent of soft soap. It usually occurs as a transparent jelly, but may be dried to a friable, deliquescent powder. It dissolves in alcohol or in a little water, but in presence of excess of water gives free alkali and a gelatinous acid oleate insoluble in water, but soluble in alcohol. It may be prepared similarly to the sodium salt.

Ammonium oleate $C_{18}H_{33}O_2NH_4$, a gelatinous substance soluble in water; may be prepared by treating oleic acid with cold aqueous ammonia.

Calcium oleate $(C_{18}H_{33}O_2)_2Ca$ is the lime soap obtained, as previously described, in the saponification of olein. It is a white bulky precipitate insoluble in water but soluble in glycerin.

Barium oleate $(C_{18}H_{33}O_2)_2Ba$ separates as a bulky white crystalline powder from an alcoholic solution.

Magnesium oleate $(C_{18}H_{33}O_2)_2Mg$ is a soft, granular powder.

Aluminium oleate has been described under aluminium salts (*v.* ALUMINIUM).

Ferric oleate is a dark-red substance similar to the aluminium salt.

Copper oleate $(C_{18}H_{33}O_2)Cu$ is a fine green salt soluble to an oily solution in a little alcohol, and fusible below 100°.

Mercuric oleate (the *oleatum hydrargyri* of the Pharmacopœia) $(C_{18}H_{33}O_2)_2Hg$ is a white greasy solid, sparingly soluble in cold alcohol, readily dissolved by strong alcohol and ether.

For medicinal purposes it is prepared as a solution in excess of oleic acid by gradually adding 1 part of the yellow oxide to 9 parts of oleic acid with constant stirring and trituration until the whole is dissolved. It then forms a light-brown semi-solid grease. It may be prepared with half the above quantity of oleic acid, the remainder being added shortly before use.

Zinc oleate (*oleatum zinci*) $(C_{18}H_{32}O_2)_2Zn$ is a white greasy powder, soluble in carbon bisulphide and petroleum spirit, and fusible below 100°. The medicinal preparation is made by stirring together 1 part of zinc oxide and 9 parts of oleic acid, and, after two hours, heating on the water-bath until the oxide has dissolved. Ointment of zinc oleate is prepared by mixing equal parts of this preparation and soft paraffin.

Lead oleate $(C_{18}H_{32}O_2)_2Pb$, the principal constituent of 'lead plaster,' may be obtained by the addition of an aqueous solution of sodium oleate to a solution of lead acetate containing sufficient acetic acid to render the solution clear. It is a white powder melting at 80° to a yellow oil, which solidifies to a brittle mass. It dissolves in alcohol, ether, turpentine, and petroleum spirit. A basic oleate nearly insoluble in ether is obtained by boiling oleic acid or an oleate with excess of litharge.

Oleates of *veratrine*, *morphine*, *aconitine*, *quinine*, &c., are prepared for medicinal use by dissolving the alkaloid in oleic acid. The first three contain 2 parts of the alkaloid to 98 parts of the acid, and are thus really solutions of the salt in oleic acid. Quinine oleate is prepared by triturating, with the acid of gentle heat, 25 parts of quinine in 75 parts of the acid.

Oleates of glycerin (*v.* OLEIN).

OLEIN. This term is applied commercially to any liquid oil obtained from partly solid oils by pressure. True olein is the glyceride of oleic acid, and occurs in most liquid and solid fats such as non-drying oils, almond, olive, and cod-liver oil, lard, tallow, palm oil, butter, &c. It is largely prepared in the manufacture of margarine and in other industries (*v.* MARGARINE). The product of the cold pressing of cocoanut and palm oil is known as 'cocoanut olein' and 'palm olein' respectively, the former resembling tallow, and being used in the manufacture of night-lights and soap.

The term 'olein' is also applied to crude oleic acid and to the sodium, potassium, or ammonium salt of the sulphonate of oleic acid used in dyeing cotton goods with alizarin (*v.* OLEIC ACID). The sulphonate of ricinoleic acid similarly prepared from castor oil is also known as 'olein.'

Three true oleins exist:

Monolein $C_3H_5(C_{18}H_{33}O_2)(HO)_2$,
Diolein $C_3H_5(C_{18}H_{33}O_2)_2HO$,
Triolein $C_3H_5(C_{18}H_{33}O_2)_3$.

The latter, which is the only one occurring naturally, constitutes the olein of oils and fats.

Triolein may be prepared by heating a mixture of equal parts of glycerin and oleic acid at 200°, decanting the fatty matter after the reaction finishes, mixing with 15 to 20 parts by weight of oleic acid, and re-heating to 240° in a sealed tube for three or four hours. The mass is treated with lime and ether, thus dissolving out the triolein while the unchanged oleic acid becomes changed into the lime salt. The solution is decolourised with animal charcoal and mixed with eight volumes of ordinary alcohol, and the precipitated triolein is dried *in vacuo*.

Triolein may also be prepared by cooling almond or olive oil to 0°, removing the liquid parts by pressure, dissolving in three volumes of hot alcohol, and crystallising out at 0°. The alcohol is removed from the crystals by agitation with water.

For methods of obtaining olein commercially *v.* MARGARINE.

Monolein is prepared by heating oleic acid with excess of glycerin in a sealed tube for 24 hours at 200°, while diolein is similarly obtained by heating triolein with a proper proportion of glycerin. Monolein is an oily liquid slowly solidifying at about 15°. It is only slowly saponified by lead oxide. Diolein solidifies at about the same temperature.

Triolein is a colourless, odourless, tasteless oil capable of being distilled *in vacuo*, and remaining liquid even below 0°. It is insoluble in water and only slightly soluble in alcohol, but dissolves abundantly in ether. On exposure to air it becomes acid and rancid, and darkens in colour.

OLEOMARGARINE, MANUFACTURE OF. This description is taken from the Report of the Commissioner of Internal Revenue of America. The ingredients used are: Oleo oil, neutral lard, some liquid vegetable oil, as cotton-seed, sesamé or peanut, butter in the higher grades, cream and milk, together with salt and annatto, or other colouring matter.

The manufacturer of oleomargarine usually buys the refined materials in the open market. The manufacture of oleo oil is generally carried on in connection with the large slaughter- and packing-houses situated in or near the principal cities. The caul and suet fats are removed from the freshly slaughtered beeves and placed in tanks filled with water at 75° to 85°F., where they remain from two to three hours before being transferred to other tanks containing iced water. By this procedure the fats are gradually deprived of their animal heat, and the danger of their becoming rancid is avoided, as would happen if the mass of fat were suddenly chilled by being placed directly in iced water. The caul, long or slaughter fat, is kept separate from the suet fat, which yields an inferior grade of oil. A Texan steer will yield on an average 65 lb. of caul and suet fats, from which are obtained 28 lb. (43 per cent.) of oleo oil, 21 lb. (32 per cent.) of oleo-stearin, and 12 lb. (20 per cent.) of high-grade tallow. The chilled fat, after thorough washing from blood, is fed into hashers working at high speed, from which it issues through fine sieves into the rendering tank. No fat remains on hand longer than 14 hours, usually not more than four hours, before being rendered. The rendering tank is a steam-jacketed upright kettle of 2,000 to 5,000 lbs. capacity, provided with revolving blades. Steam being let into the jacket, the hashed fat is continuously fed in and kept in motion by the stirrer. When the tank is full and the contents thoroughly melted, the temperature being 120° to 150°F., the fat is allowed to rest for the water and scrap to settle.

The clear fat is drawn off from the top and run into the graining or seeding cars of 400 to 600 lbs. capacity. The temperature of the room in which these cars are stored is maintained at 85° to 95° F., and the whole contents of the car will be in a semi-solid condition in from one to three days. This fat is free from all 'greasy' taste. It is now taken to the press-room, kept at 70° to 80° F., where it is ladled out on a stout linen cloth, which is folded up ready for placing in the screw-press. When the press is filled, pressure is gradually applied, and the expressed oil constitutes the 'oleo oil.' This liquid fat is allowed to cool in barrels, and at ordinary temperature forms a soft, granular, tasteless, and nearly colourless fat. The hard fat remaining in the filter bags forms the beef or oleo-stearin, which is used for making 'refined lard' by the addition of cotton-seed oil, or is sold to the soap and candle maker.

The manufacture of 'neutral lard' is conducted by essentially the same machinery and at about the same temperatures as for oleo oil, but only the leaf fat of freshly slaughtered hogs is used. A hog yields from 5 to 15 lbs. of leaf lard, of which 100 lbs. yields 90 lbs. of 'neutral.' The screw-press is not employed to separate the stearin, but the melted fat is run directly from the rendering tank into a very strong iced brine, where it remains for 24 hours before being placed on shelves to drain. The 'neutral' is a white, slightly granular, tasteless, solid fat.

The by-products of the oleo oil and neutral lard manufacture—namely, stearin, tallow, and lard—are standard merchantable articles. Only fresh and sweet fats are used, and great cleanliness is observed through all the processes. The vegetable oils employed are refined by ordinary methods, whereby a product of a light straw-colour and bland taste is obtained. The butter used is always selected for its high flavour. The granular character of oleo oil requires the addition of a softer fat, such as neutral lard or cotton seed or other vegetable oil, in order to approach more closely to the consistency of butter. The proportions in which these ingredients are used vary with the season of the year, the grade desired, and the formula of the manufacturers. The charge of milk or cream, however, is the same for all grades manufactured in some factories, and varies from 10 to 20 per cent. The milk or cream is allowed to become slightly sour. The mixing of the materials to form the butter substitute is conducted in a steam-jacketed churn for from 1,200 to 2,500 lbs. capacity. The oleo oil and neutral lard are melted in separate vessels at 90°F. The charge of milk or cream is first run into the churn, and the paddles are kept in motion until the butter begins to form. Then the oleo oil is added and stirred, next the neutral lard, and finally the annatto to give the desired colour. The butter is either added to the churn or worked in subsequently. The temperature is carefully regulated, beginning at about 85°F. and increasing gradually to 105° F. at the end of the operation, when the whole charge has the appearance of a yellowish-creamy fluid. From 20 to 90 minutes are occupied in the churning. The finished charge is run into tanks containing chopped ice and constantly stirred, or is met by a stream of iced water as it issues from the churn, the object being to give the mass a fine grain by the sudden cooling. The chilled mass is then placed on wooden trays to drain. Here the salt is added and allowed to work itself in, which generally takes from 12 to 24 hours. The salted mass is then thoroughly worked by mechanical rollers to remove the buttermilk and water.

Oleomargarine is placed on the market either 'solid packed' or in prints or rolls. Four grades are generally made, known as 'dairy' and 'extra dairy oleomargarine,' 'creamery' and 'extra creamery butterine,' the last two containing from 10 to 25 per cent. of the best creamery butter. In the lower grades from 25 to 60 per cent. of neutral lard, 20 to 50 per cent. of oleo oil, 5 to 25 per cent. of vegetable oils, and in some cases from 2 to 10 per cent. of butter, with 10 to 20 per cent. of milk or cream, are the proportions used. Some factories employ no vegetable oils in their oleomargarine, preferring to use a larger proportion of neutral lard with a small amount of butter to obtain the desired butter consistency. In the higher grades the proportions of oleo oil are reduced, the vegetable oils are discarded, and creamery butter is used to make up the charge (Eng. and Min. Jour. 47, 210–212; S. C. I. 8, 408) (*v.* Margarine).

OLEO-RESINS. Under the generic term oleo-resins are here described the chief representatives of that large group of natural products the essential constituents of which are resin and volatile oil. These substances are mostly the oleo-resinous juices of plants more or less deprived of their volatile oil by evaporation, but still retaining enough to rank as one of their two leading components. For a more detailed list of oleo-resins such works as Watts's translation of Gmelin's Handbook, the numerous reports on botanical economics, and the catalogues of the various museums, should be consulted. Compare also introduction to article Resins.

Copaiba. *Oleo-resin copaiba*; *Balsam of copaiba or copaiva or capivi*; *Baume ou oléo-résine de copahu*, Fr.; *Copaiva balsam*, Ger. Copaiba is the oleo-resinous secretion of the trees of the genus *Copaifera*, especially the species *C. Langsdorfii* (Desf.), which inhabit the warmer districts of South America. Descriptions of the leading species yielding the so-called balsam are given by Flückiger and Hanbury (Fl. a. H. 227) and Bentl. a. T. 93. The drug became known in Europe in the seventeenth century, and was included in the Amsterdam Pharmacopœia of 1636 and the London Pharmacopœia of 1677. The yield of oleo-resin from a single tree is very great, the ducts containing it distending sometimes to such an extent as to burst the unyielding trunk with a report which is heard at long distances. In commerce the Pará variety is distinguished from that coming from Maranham and from the rarer Maracaibo copaiba.

In trade the oleo-resin occurs as a transparent, rarely opalescent, viscid liquid of a pale-yellow or light golden-brown colour, and a characteristic aromatic, not disagreeable, odour and persistent acrid bitterish taste. The specific gravity, which varies with variation in the proportion of oil present, is generally 0·94 to 0·993.

Alcohol, benzene, bisulphide of carbon, and acetone dissolve most specimens of copaiba. Glacial acetic acid dissolves the resin only. When mixed with small quantities of magnesia, lime, or baryta, most specimens form a stiff mixture which gradually hardens. This depends upon the presence of an acid resin which forms solid combinations with alkaline earth metals. Flückiger (Jahresb. Pharm. 1867, 162, 1868, 140) finds the action of copaiba on polarised light to vary, some specimens being dextro- and others lævorotatory.

According to Umney (Ph. [3] 8, 252), the *volatile oil* in copaiba varies from 20 to 60 p.c., the percentage of *resins*, which are the sole other constituents, showing corresponding differences. Numerous analyses of copaiba are recorded. Among the older observers are F. Hofmann, 1748 (Obs. Phys. Chym. lib. 1, obs. 6); Schoenberg (Pfaff, Mat. Med. iv. 12); Stoltze (B. J. [27] 2, 179) and Gerber (J. Ph. 16, 79, a. 367).

Volatile oil of copaiba or *copaivene* $C_{20}H_{32}$ is an isomeride of oil of turpentine. It boils at 252–256°, is soluble in 8 to 30 parts of alcohol (sp.gr. 0·830), or in 3 parts of absolute alcohol, and has a specific gravity of 0·88 to 0·91. The oil has the odour and taste of copaiba. When hydrochloric acid gas is passed through the dried oil, crystals of *copaivene hydrochloride* $C_{20}H_{32}4HCl$ are formed (Levy a. Engländer, A. 242, 191). *Cf.* Bonastre (J. Ph. 11, 529); Ader (J. Ph. 15, 95); Gerber (Br. Arch. 30, 157); Blanchet (A. 7, 156); Soubeiran and Capitaine (J. Ph. 26, 70); Aubergier (J. Ph. 17, 278); Gerhardt (C. R. 17, 314); Chautard (C. R. 34, 485); and Posselt (A. 69, 67). The terpene of Maracaibo copaiba boils at 250–260°, and gives no crystalline hydrochloride (Brix, M. 2, 507). A dark-blue *hydrate* $(C_{20}H_{32})_3H_2O$ is obtained towards the end of the operation when the moist terpene is distilled over sodium (Brix).

Of the copaiba resins many are found only in certain varieties of the oleo-resin. The most important is the crystalline acid resin *copaivic acid* $C_{20}H_{30}O_2$. This constitutes by far the greater portion of the crude resin, and may be obtained according to Schweitzer (P. 17, 784; 21, 172) by dissolving the resins in aqueous ammonia and setting aside at a temperature of −10°, when it comes out in the form of crystals. Copaivic acid was further studied by Rose (P. 33, 83; A. 13, 177; 40, 310) and Hess (A. 29, 140) when the formula was established. The acid is an isomeride of abietic acid. Crystalline deposits sometimes occur in copaiba. One of these, in an old specimen of the Trinidad variety, which was supposed to be copaivic acid was examined by Flückiger and Hanbury (Fl. a. H. 231). It melted at 116°–117°. Another deposit investigated by Fehling (A. 40, 110) proved to be an allied compound *oxycopaivic acid* $C_{20}H_{28}O_3$. Similarly Strauss (A. 148, 148) extracted *metacopaivic acid* $C_{22}H_{34}O_4$ from Maracaibo copaiba. This variety of copaiba has been re-investigated by Brix. Other *resins* have been described by Martin and Vigne (J. Ph. 1842, 52), Posselt (A. 69, 67), and Rush (Am. J. Pharm. (4), 9, 305), but they need further investigation. *Cf.* Oberdöfer (Ar. Ph. [2] 44, 172); Ulek (Ar. Ph. 122, 14); Stockhardt (Ar. Ph. 38, 12); Procter (Ph. 10, 603); Roussin (J. Ph. [4] 1, 321); Levy (B. 18, 3206).

In medicine copaiba is employed for its stimulating action on mucous membranes, especially those of the genito-urinary system.

Adulteration of copaiba has been largely practised. Turpentine, castor oil, and Gurjun 'balsam' are typical of the adulterants employed. Numerous methods of testing have been proposed. These are reviewed by Siebold (Ph. [3] 8, 251). It is shown that the specific gravity or percentage of resin and oil is so variable as to be of no value in detecting adulteration. Many properties while appertaining to most specimens of the oleo-resin do not hold true of them all. Thus fluorescence, a character of gurjun 'balsam,' is not absent from all specimens of true copaiba; all specimens do not dissolve one-fourth of their weight of magnesium carbonate or form a clear solution with aqueous ammonia or alcohol. Benzene is a universal solvent for copaiba, but it behaves in the same manner toward all the ordinary adulterants. Muter (An. 1, 160) devised a method for the 'detection of castor oil and other fats,' depending upon the separation of their sodium salts, but Siebold considers the following simpler method much more delicate. A gram or so is heated in a watch-glass until all oil is driven off, which is the case as soon as the residue assumes a rich-brown colour. If the remaining resin is brittle and pulverisable no fatty oil is present. As little as 1 p.c. of oil can thus be detected. Gurjun or wood oil may be discovered by Flückiger's process (Fl. a. H. 233 note). One drop of copaiba is agitated in a test tube with 19 drops of carbon bisulphide, and to this is added a drop of a mixture of equal volumes of strong sulphuric and nitric (1·42) acids. After a little agitation copaiba becomes reddish-brown with a deposit of resin on the sides of the tube; gurjun oil gives an intense purplish-red colour changing to violet, while the oleo-resin of *Hardwickia*, sometimes an adulterant of copaiba, gives no perceptible alteration of colour. By this procedure 1 part of gurjun oil in 8 parts of copaiba may be detected. Another method is that of Hager (Ph. Centh. 16, 257). 1 volume of copaiba mixed with 4 volumes of petroleum ether gives either a clear solution or only a slight turbidity, which when it settles forms not more than a thin film covering the bottom of the vessel. Gurjun oil is insoluble in petroleum ether and settles in half an hour. Benzene cannot be substituted, as has been proposed, for petroleum ether. The German Pharmacopœia tests copaiba by shaking 1 part with 5 parts of water at 50°, when a turbid mixture should result, and this warmed on a water-bath should separate again into two clear layers. This is not the case when 10 p.c. of gurjun 'balsam' is present. The presence of oil of turpentine is recognised by Siebold during the evaporation for the detection of fixed oils, and may be further identified by distillation and fractionation of the volatile oil. Turpentine boils at 70°, oil of copaiba at 240°–250°. See further: Bowman (Am. J. Pharm. [4] 7, 385); Fulton (Am. J. Pharm. [4] 7, 550); Rush (Ph. [3] 10, 5); Hager (Ph. Centh. 1870, 296; 24, 141); Prael (Ar. Ph. [3] 23, 735 a. 769); Wayne (Am. J. Pharm. [4] 3, 326).

Elemi. *Oleo-resina elemi*; *Résine elémi*, Fr.; *Elemiharz*, Ger. The Greek and Roman writers describe a 'gum of Ethiopian olive' which has been generally identified with elemi. According to Flückiger and Hanbury (Fl. a. H. 147), however, this ancient elemi is the oleo-resin known as *Luban meyeti.* Pliny terms the drug *enhæmon* or *enhæmi*, from which the name *animi* and perhaps also *elemi* is derived. The term 'animi' is also used for a kind of copal.

During the 16th century the older African elemi was replaced by a drug of similar appearance, which came from Mexico and South America, and this in its turn has given way to a product of the Philippine Islands, which is now the elemi of the British and German Pharmacopœias.

Elemi or Animi of the older Writers; Oriental or African Elemi; Luban Meyeti; Luban Mati.

This drug is derived from *Boswellia Frereana* (Birdwood), a tree belonging to the same genus which yields the gum-resin olibanum, and which inhabits the hills immediately west of Cape Gardafui. Notwithstanding the close botanical relation to olibanum, and the generic name Luban being Arabic for that drug, there is no doubt, owing to the entire absence of gum and other characters, that Luban Meyeti is a distinct product. According to Hanbury and Flückiger (Ph. [3] 8, 805; Fl. and H. 147), this was the elemi of commerce until its place was taken, in the 16th century, by a somewhat similar product of Mexico and South America. It is mentioned by Wellsted (Travels in Arabia) in 1838.

Luban elemi is described by Flückiger and Hanbury as detached droppy tears and fragments, occasionally in stalactitic masses several ounces in weight. Externally it has a thin opaque white crust, but internally it is transparent and of an amber colour. It has an agreeable odour of lemon and turpentine, and a mild terebinthinous taste. The *volatile oil*, which has a fragrant elemi odour, from the specimen examined, amounted to 3·1 p.c. It has a specific gravity of 0·856 at 17°, and rotates the polarised ray slightly to the left. It consists partly of a *dextrogyre hydrocarbon* $C_{10}H_{16}$, and partly of a *lævogyre oxygenated oil.* The *resin* is mostly soluble in alcohol, and has the composition $C_{20}H_{30}O_2$.

Elemi of the 17th–18th Centuries.—American or Brazilian Elemi.

The oleo-resin which replaced the older African elemi for the most part during the 17th and 18th centuries was the product of several Brazilian trees, species of the genus *Icica.* A specimen examined by Flückiger and Hanbury (Fl. and H. 152) was a translucent greenish-yellow fragrant terebinthinous resin, which by means of cold spirits of wine could be separated into two portions—the one soluble, and the other, consisting of a mass of acicular crystals, insoluble. Scribe (A. Ch. [3] 13, 166) investigated one of the icica oleo-resins which had lost all its volatile oil, and consisted of three neutral compounds, which he separated by the difference of their solubility in alcohol. From the alcoholic solution *brean* first comes out in white pearly stellate needles melting at 157°. Brean has the composition C 83·92 p.c., H 11·82 p.c., and O 4·26 p.c. In sulphuric acid it dissolves with a red colour. Further concentration of the alcoholic solution yields crystals of *icican*, which contain 82·01 p.c., H 11·64, and O 6·35 p.c. From the mother-liquor a small quantity of an amorphous resin, *colophon*, was obtained.

More recently the oleo-resin of *Icica heptaphylla* (Aub.) has been examined by Stenhouse and Groves (C. J. 1876, 175). This is known as *Gum Hyawa*, or *Conima resin*, or *resin of the incense-tree.* It possesses a fragrant balsamic odour, which depends on the presence of a small proportion of *volatile oil.* This oil, when obtained by distillation with steam, boils at about 270°. By treatment with sodium and fractional distillation, it gives a hydrocarbon *conimene*, $C_{15}H_{24}$, which boils at 264°. The residue after removal of the volatile oil dissolved in hot alcohol deposits on cooling a crystalline compound, *icacin*, $C_{46}H_{76}O$, and the mother-liquor contains a yellow *amorphous resin.* Icacin melts at 175° (*cf.* Hesse, A. 192, 181). A comparison of the analytical numbers, melting-points, and other characters, points to the probability that while the icican of Scribe is only an impure form of that observer's brean, this, in its turn, is the icacin of Stenhouse and Groves in an imperfect condition of purity. The amorphous resin of the latter observers is also probably the colophan of Scribe. At all events, the evidence of the existence of brean and icican needs revision.

Elemi of the present Pharmacopœias; Manilla Elemi; Arbol a Brea Resin.

The tree which yields the elemi of the present day is a native of the Philippine Islands, and is called by the Spaniards *Arbol a brea.* Its botanical relations are still uncertain, but it probably belongs to the natural order *Burseraceæ.* Manilla elemi is a soft oleo-resin which, in appearance, resembles old honey. It occurs in commerce generally admixed with earthy or carbonaceous matter, which gives it a dark colour. When fresh and pure, it is colourless; the odour is fragrant, suggestive of fennel and lemon, with a terebinthinous admixture. Cold spirits of wine applied to the drug discloses numerous acicular crystals visible under a microscope (Fl. and H.).

Elemi is a mixture of *volatile oil* and *resin.* Bonastre (J. Ph. 10, 199) obtained 12·5 p.c. of volatile oil; Stenhouse (A. 35, 304) 3·5 p.c.; H. Sainte Claire Deville (C. R. 12, 184) in good specimens 13 p.c.; and Flückiger and Hanbury (*loc. cit.*) 10 p.c. The oil is fragrant, colourless, and neutral, and has the constitution $C_{10}H_{16}$. Its specific gravity is 0·852 at 24° (St.), 0·849 at 11° (D.), 0·861 at 15° (Fl. and H.). The boiling-point is 166° (St.) or 174° (D.), and Deville finds the vapour density to be 4 (*cf.* Wallach (A. 252, 94). The same observer notes that the oil is lævogyre, and that it gives a crystalline *hydrochloride* $C_{10}H_{16}2HCl$. The crude oil examined by Flückiger and Hanbury was dextrogyre, but they obtained fractions that were lævogyre. These pharmacologists were unable to obtain a crystalline hydrochloride, but, mixed in certain proportions with alcohol, nitric acid, and water, and set aside, elemi was found to deposit crystals probably identical with terpine hydrate.

The resin of elemi was first examined by Maujean (J. Ph. 9, 45), who showed that it contained two resins, one soluble in cold and the other in hot alcohol. *Cf.* Rose (A. 13, 192; 32, 297; 40, 307) and Hess (A. 29, 136). Bonastre found the former to exist to the extent of 61 p.c., and the latter, which crystallised easily, 25 p.c. Baup (A. Ch. [3] 31, 108) called the latter *amyrin*. It is insoluble in water, readily soluble in ether and hot alcohol, and crystallises in satiny fibres, which melt at 174° (Baup) or 177° (Fl. a. H.). *Cf.* Buri (N. R. P. 25, 193) and Hesse (A. 192, 180). Amyrin, $C_{30}H_{50}O$, has been converted by Vesterberg into two crystalline isomeric acetates, $C_{30}H_{49}(C_2H_3O_2)$, and benzoates, $C_{30}H_{49}(C_7H_5O_2)$, from which two corresponding amyrins have been prepared. (α)-*Amyrin* melts at 180–181°, (α)-*amyrin acetate* at 220° and *benzoate* at 192°; while (β)-*amyrin* melts at 193–194°, (β)-*amyrin acetate* at 235°, and *benzoate* at 230° (B. 20, 1243). Ciamician (B. 11, 1347), by distilling amyrin with zinc-dust, obtained *toluene*, *methylethylbenzene*, and *ethylnaphthalene*. The alcoholic mother-liquor contains the *amorphous resin*, or resin soluble in cold alcohol, which is the largest constituent of elemi. It was analysed by Johnston (A. 44, 338). Besides amyrin, Baup describes three other compounds occurring in elemi—*breïdin*, *breïn*, and *bryoïdin*. Breïn is certainly, in view of Flückiger and Hanbury's investigation, impure amyrin, and the existence of breïdin requires further proof. Bryoïdin $C_{20}H_{38}O_3$, however, may be obtained in silky crystals by extracting the elemi, after removal of the oil, with hot water. On concentration and cooling, it precipitates. It melts at 135° (B.), 133·6° (Fl. and H.), and may be sublimed. It is neutral, has a bitter taste, and while insoluble in cold water dissolves readily in hot and in alcohol and ether (Ph. [3] 5, 142).

A new crystalline substance, *elemic acid* $C_{35}H_{56}O_4$, was discovered in small proportion in elemi by Buri in 1878 (Ph. [3] 8, 601). It melts at 215° and forms crystalline salts.

Elemi is seldom used in medicine in this country. It is, however, sometimes employed in the form of ointment as a dressing for indolent ulcers.

Oleo-resins allied to Elemi.

Anime. Much confusion exists as to the use of the word anime, and the same may be remarked of tacamahac. By some writers anime is used as synonymous with elemi, and by others it is restricted chiefly to a variety of copal. There are, however, a number of other oleo-resinous products which are usually known as anime. The chief members of this class are:—1. *Gomart oleoresin*, the exudation of *Bursera gummifera* (Linn.), an inhabitant of the West Indies. This has an odour between that of elemi and turpentine. Its *volatile oil* was examined by Deville (A. Ch. 27, 90). It resembles turpentine, has the formula $C_{10}H_{16}$, and forms a crystalline hydrochloride $C_{10}H_{16}2HCl$. 2. *Brazilian anime*, the product of *Hymenæa Courbaril* (Linn.), a tree belonging to the natural order *Leguminosæ*. The oleo-resin resembles mastic. It softens in the mouth, and when warmed emits a peculiar odour. The volatile oil is colourless, with a strong, not unpleasant odour and burning taste. It is completely soluble in alcohol (Paoli, Brugn. Giorn. 16, 326). After removal of the oil, cold alcohol extracts an *amorphous resin*, and the residue, dissolved in boiling alcohol, deposits on cooling a *semi-crystalline compound*, which was analysed by Laurent (A. Ch. 66, 314). See also Batka (Ph. [3] 6, 742); Guibourt (Rév. scient. 16, 177); Filhol (J. Ph. [3] 1, 301 a. 507); Hancock (Ed. N. J. Sc. 1, 240); Manzini (J. Ph. 27, 752); Deville (A. 71, 354).

Caranna. A soft oleo-resin allied to Brazilian elemi, probably derived from *Icica Caranna* (Kunth) and allied species. It has a fragrant balsamic odour and somewhat bitter taste. It contains 96 p.c. of resin, soluble in alcohol (Pelletier, B. Ph. 4, 241).

Ceradia. The product of *Ceradia furcata*. It is an amber-coloured oleo-resin with the odour of elemi (R. Thomson, P. M. 28, 422).

Mauritius elemi. An oleo-resin very closely resembling Manilla elemi. It is the yield of the *Colophonia Mauritiana* (De Cand.; Fl. a. H. 152).

Mexican elemi. Vera Cruz elemi. Mexican elemi is not now an article of commerce. It is nearly related to Brazilian elemi. It is the product of *Amyris elemifera* (Royle; Fl. a. H. 152).

Tacamahac. The following are the more important oleo-resins which have been described as tacamahac:—1. *East Indian tacamahac*, the product of *Calophyllum inophyllum* (Linn.), which inhabits Bourbon and Madagascar. It is a dark-green balsamic resin—specific gravity 1·032; melting-point 75°. 2. *Yellow tacamahac.* This oleo-resin is the exudation of *Amyris tacamahac* (Batka). It was labelled *Tacamahaque vierge* by Des Marchais, *African incense* by Pereira, and *Bdellium d'Afrique* by Guibourt. It melts at 100°, exhaling an agreeable odour, and the resin remaining is partly soluble in alcohol. The part insoluble in alcohol consists of yellow crystals—*tacamahacin*. This substance is insoluble in ether, sparingly soluble in alcohol, and is unaffected by alkalis or nitric acid. Sulphuric acid dissolves it with a violet colour (Batka, Ph. [3] 6, 742). Yellow tacamahac is often termed anime. 3. *Oleo-resin of Icica heptaphylla.* This has been already described under the name of *conima resin* (see *Elemi of the 17th–18th centuries*).

Besides these, which Batka regards as true tacamahacs, the product of *Bursera obtusifolia*, the *Mauritius tacamahac*, and common *galipot* of *Pinus maritima*, the latter under the name of the *bitter tacamahac of trees*, have been described as varieties of that drug.

Gurjun oleo-resin. *Gurjun balsam*; *Wood oil*; *Oleo-resina dipterocarpi.* This oleo-resin resembles and is used as an adulterant and substitute for copaiba. It is obtained from Burma and the Straits, being the product of various species of *Dipterocarpus* (Fl. a. H. 88). Gurjun oil must not be confounded with the fatty oil which is also known as wood oil, or *wood oil of China*, which is expressed from the seeds of the

Aleurites cordata (Müller), the well-known *Tung* tree of the Chinese.

Gurjun, or wood oil, resembles copaiba in appearance, with the exception of its fluorescence, a character rarely found in copaiba. When heated in a closed tube to 220° it becomes almost solid, whereas copaiba similarly heated does not lose its fluidity. For other distinguishing characters *v.* COPAIBA.

Wood oil was noticed by Lowe (Ph. 13, 65); Hanbury (Ph. 15, 321); Martius (N. R. P. 5, 100), Guibourt (N. R. P. 6, 97), and Hirschsohn (Ph. [3] 10, 561). Werner (Z. 1862, 588) found it to consist of 20 p.c. of *volatile oil* $C_{20}H_{32}$, a polymeride of turpentine, and a residual *resin* which contained *gurjunic acid* $C_{44}H_{68}O_8$, a crystalline compound soluble in aqueous ammonia. Other observers have found different percentages of oil and resin, which are indeed very variable. The volatile oil boils at 255°–260° (Fl. a. H.), 255° (W.), and its specific gravity is 0·915 (Fl. a. H.); 0·904 (W.); 0·928 (De Vry, Ph. 16, 374). Amylic alcohol dissolves the volatile oil, but it is only sparingly soluble in ethylic alcohol and glacial acetic acid. The hydrocarbon is coloured a magnificent blue by hydrochloric acid, but does not form a crystalline hydrochloride. It is lævogyre (W.); dextrogyre (Fl. a. H.).

The resin of wood oil is extracted by alcohol and aqueous solution of ammonia added, and the *amorphous resin* which separates collected. The solution contains *ammonium gurjunate* from which gurjunic acid is obtained as a precipitate on the addition of a mineral acid, and it may then be recrystallised from ether or alcohol. Werner found it to melt at 220°, and to boil with decomposition at 260°. Gurjunic acid is soluble in alcohol, benzene, and carbon bisulphide. It may be regarded as tri-hydrated abietic acid thus:—$C_{44}H_{64}O_5 3H_2O$. This formula agrees equally well with Werner's data (Fl. a. H.). It is probably identical with the meta-copaibic acid of Strauss (*v.* COPAIBA). A *compound*, $C_{20}H_{30}O_2$, yielding a diacetate is obtained from gurjun oleo-resin and enters commerce as 'copaivic acid.' It is crystalline, melts at 126–129°, is soluble in alcohol and ether but insoluble in water and alkalis (Brix, M. 2, 516). The amorphous resin which constitutes the chief part of the resin of wood oil has not been further studied.

In addition to its use as a substitute for copaiba, wood oil is employed in India as a natural varnish, especially for ships.

Labdanum; *Ladanum.* A sticky, black-brown, soft oleo-resin, derived from *Cistus creticus* (L.) and other species of *Cistus*, inhabiting the Grecian Archipelago and the shores of the Mediterranean (*cf.* Bentl. a. T. 24). It is a variable mixture of resin, volatile oil, gum, wax, and earthy and woody impurities. The odour is fragrant, and it has a bitter taste. Guibourt (Hist. Drogues, 3, 601), Pelletier (Bl. Ph. 4, 503), Johnston (Tr. 1840, 344), Thiselton Dyer (Ph. [3] 15, 301; 16, 385 and 779).

Lupulin. *Lupulinic glands*, *Lupulina*, *Lupuline*, Fr.; *Hopfendrüsen*, *Hopfenstaub*, Ger. The detached minute glands of the strobile of *Humulus Lupulus* (Linn.) contain *volatile oil*, a *bitter acid*, *resin*, *wax*, and possibly an *alkaloid.*

The volatile oil which exists to the extent of about 0·9 p.c. (Fl. a. H. 553) consists according to Wagner (J. 1853, 516) and Personne (J. Ph. [3] 26, 241 a. 321; 27, 22; J. 1854, 654) of a *terpene*, $C_{10}H_{16}$, boiling at 175°, and an oxygenated compound probably *valerol*, $C_6H_{10}O$, which boils at 210° and on oxidation yields *isovalerianic acid.* The latter acid has also been detected in hops. The crude oil boils from 140–300°. *Cf.* Mehu (Thèse, Montpellier, 1867), and Ossipow (J. pr. [2] 28, 448). The investigations of Lermer (J. pr. 101, 137) and Bungener (Bl. 45, 489) have shown that lupulin contains a crystalline compound *lupulinic acid* or *hopfenbittersäure* $C_{50}H_{70}O_8$ (?), which by the action of air and moisture changes into an amorphous substance identical with the *bitter constituent of hops.* To prepare lupulinic acid lupulin is extracted with ligroin and the crude crystals which are obtained on concentrating the solution are purified by recrystallisation from alcohol and afterwards from ligroin. The acid crystallises from ligroin in prisms which melt at 92–93°. It is insoluble in water, soluble in ligroin, and very soluble in alcohol, ether, benzene, chloroform and carbon bisulphide. It oxidises readily, reduces ammoniacal silver solution and forms a compound with copper. According to Lermer lupulin may consist of myricylic palmitate and the same observer obtained evidence of the presence of an alkaloid in the glands. Hop-resin is tasteless, and combines with metals. Compare Griesmayer (Am. J. Pharm. 1874, 360), Sarrazén (J. Ph. 1876, 437), Bissell (Am. J. Pharm. 1877, 582), Etti (D. P. J. 228, 354), Siewert (B. C. 1879, 54), Issleib (Ph. [3] 11, 6), Ladenburg (B. 19, 783), Paul (Ph. [3] 16, 877).

Mecca or **Opobalsam.** *Balm of Gilead.* This oleo-resin is the balm of the Old Testament and the Greek writers, and is the substance to which the name 'balsam' was originally applied. The term has, however, with the advance of discovery, come to have another meaning, and is now employed in a generic sense for those resins, oleo-resins, or gum-resins which contain cinnamic or benzoic acids (compare BALSAMS). Mecca oleo-resin is the product of *Balsamodendron Opobalsamum* (Kunth), a tree growing in Arabia. Trommsdorff (N. J. T. 16, 62) finds it to consist of *volatile oil* 30 p.c., *soft resin insoluble in alcohol*, 4 p.c.; *hard resin soluble in alcohol*, 64 p.c.; *extractive and loss*, 2 p.c. A specimen analysed by Bonastre (J. Ph. 18, 95) contained only 10 p.c. of volatile oil, and the other constituents were correspondingly higher. In physiological action the oleo-resin is allied to copaiba and the turpentines.

Hardwickia pinnata oleo-resin. This oleo-resin is an Indian substitute for copaiba. It is derived from a tree nearly related to the *Copaifera*, which inhabits the forests of South Travancore Ghats and South Canara. A specimen examined by Flückiger and Hanbury (Fl. a. H. 233) was a thick, black-looking, viscid fluid, which, when viewed by transmitted light in thin layers, was yellow-green or vinous red according to the thickness. It had no fluorescence, nor was it gelatinised by heating, as is the case with wood oil. Broughton (Beddows, Flora Sylv. S. India, Madras, 1872, 255) found 25 to 40 p.c. of *volatile oil* $(C_5H_8)_n$, boiling at 225°. From the resins this observer was unable to prepare copaivic acid.

Minjak-lagam. An oleo-resin resembling gurjun, the product of an unknown tree in Sumatra, has been examined by Haussner (Ar. Ph. 21, 241). It is dingy green by reflected and yellow by transmitted light. It is soluble in alcohol, ether, benzol, chloroform, and carbon bisulphide, and yields 33 p.c. of *volatile oil* $C_{20}H_{32}$, boiling at 250°. The *resin* is composed of an acid $C_7H_{14}O_3$ and a neutral constituent.

Sumbul oleo-resin. *Racine de sumbul*, Fr.; *Sumbulwurzel, Moschuswurzel*, Ger. The root of *Ferula Sumbul* (Hooker), or musk root (Bentl. a. T. 131), a perennial plant, inhabiting the mountains of Maghian, in the Khanate of Bokhara. When extracted with ether it yields about 9 p.c. of a *resin*, having a musky odour and $\frac{1}{3}$ p.c. of a bluish *volatile oil*.

Reinsch (J. Ph. 6, 300; 7, 79; 13, 68), by dissolving the resin in alkali and precipitating with water, obtained a salt of *sumbulamic acid*, together with some *angelate*, the two being separated by the easier solubility of the latter in water. Free sumbulamic acid is a turpentine-like mass, which assumes the form of soft yellow needles on standing. Compare also Reinsch and Riecker (Jarhb. pr. Ph. 16, 12). The existence of an alkaloid *sumbuline* in the resin has not been confirmed (*cf.* Murawieff (Dub. Quart. J. 1852, 255). Sommer (Ar. Ph. 138, 1) investigated sumbul root. On dry distillation the oleo-resin gives first a *greenish mobile oil*, smelling like creosote, then a *blue oil*, lighter than water, and with a peculiar, not very agreeable, odour. Together with these the same observer found crystals of *umbelliferone*.

Turpentine. The oleo-resinous exudates of various species of *Coniferæ*.

Crude or common turpentine. This is derived in Russia and Finland from the *Pinus sylvestris* (Linn.), or Scotch pine; in Austria and Corsica from *P. Laricio* (Poiret); in South-Western France from *P. Pinaster* (Solander); and in the United States from *P. australis* (Michaux), the swamp pine and the Loblolly pine, *P. Tæda* (Linn.) (Fl. a. H. 604; Bentl. a. T. 256–259). For concreted French turpentine, common frankincense or galipot, see Resins.

Canada turpentine, Canada balsam, Balsam of fir. A product of the balsam or balm of Gilead fir, the *Pinus balsamea* (Linn.). This is incorrectly called balsam, and it must not be confounded with true balm of Gilead or Mecca balsam (*cf.* Fl. a. H. 612; Bentl. a. T. 263).

Venice turpentine, Larch turpentine. The exudate of the larch or *Pinus Larix* (Linn.), mostly obtained from the Tyrol.

Strassburg turpentine is the yield of the Silver fir, *Sapin*, Fr., *Weisstanne* or *Edeltanne*, Ger., *Pinus Picea* (Linn.). The market is supplied chiefly from the Vosges (Fl. a. H. 615; Bentl. a. T. 262).

Hungarian turpentine is obtained from the *Pinus Pumilio* (Hänke).

Chian turpentine is the turpentine of the older writers, and is derived from a small tree, *Pistacia terebinthus* (Linn.), which inhabits the shores of the Mediterranean and Asia Minor (*v.* Turpentine).

Tar *v.* Turpentine. A. S.

OLEUM ANIMALE EMPYREUMATICUM *v.* Bone oil.

OLEUM CORNU CERVI *v.* Bone oil.

OLEUM DIPPELII *v.* Bone oil.

OLIBANUM *v.* Gum-resins.

OLIBENE *v.* Gum-resins.

OLIGOCLASE. A lime-soda plagioclase *v.* Felspar.

OLIVE OIL *v.* Oils, fixed.

OLYMPIAN GREEN. *Emerald green v.* Pigments.

OMEIRE. A drink resembling koumiss, prepared by the natives in South-West Africa by filling gourd bottles, which contain some fermented milk, with milk, shaking well and allowing to stand. Is a thick, semi-coagulated liquid, possessing a pleasant, wine-like smell, and a slightly sour taste; it contains a little alcohol (Ar. Ph. 1887. 744).

ONOFRITE *v.* Mercury; also Selenium.

ONYX *v.* Agate.

OPAL. Colloidal silica, occurring native in botryoidal and stalactitic forms, or in amorphous masses, occupying cracks and cavities in certain rocks. It is softer and less dense than quartz; its hardness being only 5·5 to 6·5, while its sp.gr. varies with the impurities present from 1·9 to 2·3. Being practically amorphous it should exhibit single refraction, but many varieties, especially of noble opal, are strongly double-refracting; the anomaly being probably due to the strain set up by unequal contraction in different directions during the solidification of the gelatinous mass. Opaline silica is nearly always hydrated, but the proportion of water varies from about 2·5 to upwards of 10 p.c. Von Kobell found that the noble opal of Hungary lost 10·94 p.c. when strongly heated. The substance is almost wholly soluble in hot solution of caustic potash.

The purest opal, known as *hyalite* or *water-opal*, occurs in colourless, transparent masses, resembling glass. *Semi-opal* is a name applied to the dull, opaque varieties, generally more or less impure. *Menilite* or *liver-opal* is a brown opaque mineral, occurring in nodules in the tertiary strata of the Paris basin, especially at Menilmontant. *Wood-opal* is simply wood fossilised with opaline silica, and retaining the ligneous structure, which produces a pleasing effect when the substance is cut and polished; hence it is used in slabs as an ornamental stone. *Hydrophane* is an opal which, when dry, is opaque and dead white, but absorbs water rapidly when moistened, and becomes transparent. A fine variety found in Colorado has been brought into use under the name of 'magic stone.' *Common opal* is a general term for any opal which does not display sufficient colour to recommend its employment for decorative purposes. According to its appearance it often receives trivial names, such as milk-opal, wax-opal, &c. It is interesting to note that tridymite is a common microscopic inclusion in such opals. *Fire-opal*, found chiefly in Mexico, exhibits a brilliant hyacinthine or orange colour, which renders it of some value in jewellery. But the finest variety of the opaline group of minerals is the *precious* or *noble opal*, a substance which is unique in exhibiting by reflected light a vivid play of iridescent colours. The cause of this phenomenon has been studied by Brewster, Crookes, Behrens, Lord Rayleigh, and others. By most authorities it has been referred to the presence of numerous microscopic pores, fissures, or striæ in the interior of the stone; but Behrens considers it due to the interposition of thin lamellæ of opaline matter having a different index of refraction from that of the matrix (Sitz. W.; Math.-naturw. Cl. 64, 1871, 519). If the colours proceed from distinct patches, like a brilliant mosaic, the stone is termed in trade *harlequin opal.* Precious opal is a mineral of very limited distribution. The oldest mines are those of Dubrick, on the eastern slope of the Labanka Mountains, in Hungary, where the opal occurs in a matrix of andesite. Slabs of matrix, or 'root of opal,' inclosing brilliant particles of the gem, are polished as ornamental stones. The Hungarian mines, which are the property of the Government, though worked by M. Goldschmidt, of Vienna, employ about 200 workmen. Opal is also found at Gracias-á-Dios, in Honduras; at Queretaro, in Mexico; and near the Barcoo river, in Queensland. The Queensland opal occurs in cracks in nodules of jaspery brown iron-ore, and is remarkable for its brilliant blue and green colours. Opals are usually cut *en cabochon*, or with a convex face, but the Queensland stone, occurring in thin layers, lends itself to cameo-work, the brown ferruginous matrix forming an effective background. The so-called 'black opals' are merely precious opal intimately associated with the dark iron-stone matrix, the colour of which may be heightened by artificial staining. F. W. R.

OPAL BLUE. *Spirit soluble blue, Gentian blue 6 B. Spirit blue O, v.* Aniline blue.

OPIAURIN. Opianic acid and phenol, when heated together with strong sulphuric acid, give rise to an intense yellow-red dye. The reaction takes place between the aldehyde group of the acid and the phenol

$$C_6H_2(OCH_3)(CO_2H)(COH) + 2C_6H_5.OH$$
$$= H_2O + C_6H_2(OCH_3)_2.(CO_2H).CH:(C_6H_4OH)_2.$$

This compound *leucopiaurin* is oxidised during the process to opiaurin $C_{22}H_{18}O_6$. The best results are obtained by stirring an intimate mixture of opianic acid and phenol into sulphuric acid (60°B.), and keeping the mixture well cooled. After 24 hours' rest the melt is thrown into a large quantity of cold water, and the precipitate, when washed and dried, freed from tarry matters by extraction with hot benzene. Opiaurin is soluble in alcohol, ether, and glacial acetic acid, insoluble in benzene and petroleum-ether. It can only be obtained in the amorphous condition. It dissolves in alkalis with a purple colour; the solution in alcoholic ammonia becomes brownish-yellow on heating, but the purple colour returns on cooling.

Sulphurous acid does not reduce it. Opianic acid reacts in a similar way with other phenols, and the reaction can be used to detect the presence of opianic acid, as also of an aldehyde group in aromatic compounds; the reagents are separately dissolved in an excess of cold sulphuric acid; on mixing the solutions the colouration takes place at once (C. Liebermann a. P. Seidler, B. 20, 873-4; S. C. I. 6, 541).

OPIUM.

Origin.—Opium is the milky juice of the unripe capsules of *Papaver somniferum* (Linn.) or opium poppy, obtained by incision and inspissated by spontaneous evaporation. The plant (*v.* Bentl. a. T. 18) is perhaps indigenous to Asia Minor and neighbouring districts of South-Eastern Europe and Western Asia; but it is now cultivated more or less throughout all temperate and sub-tropical countries. It exhibits, however, morphological differences. The two most important varieties which, according to Boissier, are cultivated for the production of opium, are *glabrum*, with subglobular capsule and ten to twelve stigmata, and *album*, with egg-shaped capsules and without apertures (Flora Orientalis, 1867, 1, 116). The former is grown in Asia Minor and Egypt, and the latter in Persia and India. But besides these varieties there are minor distinctions, the petals in the same variety differ in colour, and may be white, red, or violet, with a dark-purplish spot at the base in most cases. The seeds are white or dark-coloured, and contain from a third to half of their weight of fixed oil. The capsules are provided with a lacticiferous system from which the juice exudes when they are incised. This milky juice is present in the plant in all countries where it has been grown, and opium may be collected provided that the rainfall is not too great and the temperature neither arctic nor entirely tropical. That its production is confined for the most part to Asia Minor, Persia, India, and China, is determined by other considerations such as the value of land and the cost of labour.

History.—The drug was known early in the third century B.C. to Theophrastus. Scribonius Largus, in the first century A.D., describes the method of preparing it and remarks that it should only be made from the capsules; for, as Dioscorides, writing a little later, points out, two sorts of opium were in use at that period. One of these, the opium proper, was prepared from the capsules, and the other, 'meconium,' was extracted from the entire plant by means of a solvent. Similar accounts may be found in the works of Pliny and other Latin writers. The opium of the classical period, and indeed the only variety known till the twelfth century, was exclusively that of Asia Minor. The nations of the East appear to have learned of opium from the Arabians, and it seems probable that the use of the drug was favoured by the Mahomedan prohibition of alcohol. They are supposed to have introduced the drug into China in the ninth century. Egyptian opium, 'Opium Thebaiacum,' is mentioned by Simon Januensis about the end of the thirteenth century. At this time, and three centuries later, according to Prosper Alpinus, meconium was still prepared in the Thebaïd in Upper Egypt.

In India opium was collected early in the sixteenth century. Barbosa describes a variety produced in Cambay. Pyres, the first European ambassador to China, writing in 1516, mentions three varieties of opium, obtained respectively from Egypt, Cambay, and from the kingdom of Coûs. The last-mentioned district is Kus Behár, south-west of Bhotan in Bengal. Garcia d' Orta, a little later, remarks that Cambay opium is chiefly derived from Malwa. The opium production was a State monopoly in India under the Moguls, and after the victory of Clive at Plassy in 1757 the monopoly passed into the hands of the East India Company. The manufacture then greatly increased, and it has gone on increasing until within the last few years. It was during the seventeenth century that the first accounts reached us of the production of opium in Persia. Kämpfer found that the 'theriaka,' which had long been held in high esteem by neighbouring nations, was made by mixing the finer sorts of opium with spices.

The Chinese obtained their opium from India. Until the beginning of the eighteenth century it formed part of the return cargo of their junks. The importation was then small, and it was used almost exclusively in medicine as a remedy for dysentery. The imports did not reach 1,000 chests (Malwa chests contain one pecul, or 133⅓ lbs., Patna chests 160 lbs.) until 1767, when the trade was mostly in the hands of the Portuguese. In 1790, under the East India Company, it had become 4,054 chests. It was at this time that the habit of smoking began to spread in China. To promote the trade the East India Company established an opium depôt of two ships, which lay off the island of Macao, at the entrance to the Canton river. The importation went on increasing, notwithstanding that it was forbidden by the Chinese Government in 1796, and that an edict was issued in 1820 prohibiting opium-laden ships from entering the river. The trade, which between 1820 and 1830 had risen to 17,000 chests annually, then assumed a contraband character. Complaints, however, continued, and when in 1839 it was decided to enforce the law, this, together with other difficulties, led to a war with England which terminated in the treaty of Nanking in 1842. By this treaty five ports were opened to foreign trade, and the island of Hong Kong was ceded to the British Government. In 1859–60 the annual importation of opium from India was 54,863 chests; in 1869–70, 81,770 chests; in 1879–80, 94,836 chests; in 1884–85, 75,393 chests; in 1889–90, 70,102 chests. The decrease is due to the enormous development of Chinese production.

Numerous attempts had been made during the seventeenth and eighteenth centuries to prepare active condensed extractives from opium, but no constituent of a definite nature was discovered until the beginning of the present century. Derosne in 1803 noticed a separation of crystals on diluting an aqueous extract of opium (A. Ch. [1] 45, 257). Their basic character was demonstrated by Robiquet in 1817 (A. Ch. [2] 5, 275), and the compound is now called *narcotine*. Derosne noticed that opium solutions are precipitated by alkalis, but thought that the precipitate was the same compound which he had previously isolated. Seguin in 1814 described what was probably the chief active constituent of opium (A. Ch. [1] 92, 225). But to isolate in a definite form and make known the basic properties of *morphine* was reserved for Setürner, an apothecary of Eimbeck in Hanover, whose work extended from 1805 to 1816. During the same inquiry, in 1806, Setürner also brought to light *meconic acid* with which the morphine is combined (Am. S. 55, 72; 57, 183; 64, 65). Morphine was the first compound known belonging to the class of vegetable bases, which has since become so important; for although narcotine was isolated just before, its properties as an alkaloid were not ascertained till afterwards. Further historical and other details will be found in the article on opium in 'Pharmacographia' (Fl. a. H. 272), from which many of the facts given have been obtained.

Production.—Asia Minor. Opium is collected in Asia Minor for the most part by small peasant proprietors, the largest quantity being obtained in those countries lying to the west, and having Smyrna and Constantinople for their ports of shipment. The product of these countries is the *Turkey* opium of English commerce, and is the only kind which is official for use in medicine in this country. Of all available varieties it is the richest in morphine. The poppy grown is the variety *glabrum* of Boissier. The flowers are purplish or sometimes white, and the seeds white to deep violet. The plant grows in elevated as well as lower situations, and requires a moist soil and much attention and skill on the part of the cultivator. Details of the mode of preparing the soil and management of the crop are given by Maltass (Ph. [1] 14, 395) and Heffler (Ph. [2] 10, 434), and in the official directions drawn up by the Turkish Government for the promotion of the opium culture in Macedonia (Ph. [3] 13, 918). The crop is sometimes destroyed by early frosts, drought, or the attack of locusts. The seed is sown from November to March, and the flowering takes place from May to July. In this way successive crops of capsules become ready for incision during a period of about three months, and a saving in the cost of labour is effected.

In the course of a few days, after the petals have fallen, when the capsules are some 1½ inches in diameter, they are ready for incision. This is done transversely around the middle by means of a knife. The operation is one requiring skill, for if the incision be not deep enough an incomplete flow of juice results, and if it be too deep some of the juice is lost inside the capsule. The incisions are made in the afternoon, and the exuded and partly hardened juice is collected the following morning. It is scraped off and placed on a poppy leaf. Masses of hardened juice thus obtained are allowed to stand in the shade to dry still further, and are then made into lumps of varying size and sold to dealers in the towns. By these the opium is manipulated into cakes suitable for the market, enveloped in poppy leaves and packed in bags, into which Rumex fruits are thrown to prevent the cakes adhering together. The bags are then sealed and transmitted to Smyrna and Constantinople, where they are opened in presence of the seller, the buyer, and a public examiner. The examiner scrutinises the drug piece by piece, and by its physical characters classifies it as (1) *prime*, (2) *current*, and (3) *chiqinti*. The 'current' constitutes the great bulk of mercantile opium. An important addition to the profits of the opium culture is the sale of poppy seed, from which the oil is expressed and used for a variety of purposes. It is a bland, limpid, drying oil, of a pale colour (Maltass; Heffler; Scherzer, Ph. [3] 11, 835).

Good Smyrna opium when dry contains 12 to 15 p.c. of morphine. If less than 10 p.c. is found in a specimen adulteration may be suspected. The opium used in medicine in this country when dried is required to contain not less than 9·5 and not more than 10·5 p.c. of morphine (Brit. Pharm. 1885, 295). The dried Turkey opiums examined by Guibourt contained from 11·7 to 21·5 p.c. or a mean of 14·7 p.c. of morphine (J. 1862, 374). Of ninety-two specimens examined by Fayk Bey, the highest was 17·2 p.c., and half of them contained more than 10 p.c. (Fl. a. H.). Bulgarian opium, analysed by Theegarten, gave:—Küstendil, in large lumps, 4 to 10 oz., 17·69 p.c.; Lowtscha, 11·90 p.c.; Halitz, 7·25 p.c. (Ph. [3] 11, 896; 13, 342).

Turkey opium, as it appears in English commerce, consists of rounded masses, generally from ½ to 2 lbs. in weight but sometimes larger or smaller. Externally it is covered with poppy leaves and Rumex 'chaff.' It has a bitter taste, and peculiar, though not altogether disagreeable, odour. The following are among the more important districts, the products of which come to Constantinople:—Bogaditz; Karahissar-Sahib; Kutchaya; Balukhissar; Kurkagatsch; Ismid or Ghéve, the product of Geiveh; Beybazar; Angora; Malatia; and Tokat. In addition to these the Constantinople market receives the opium of Macedonia and, until recently at least, small supplies from Bulgaria. The cultivation of opium in Macedonia commenced in 1865 from seeds brought from Karahissar. In 1882 the districts of Kotchava, Straumnitza, and Tikvish exported 135,000lbs. by way of Salonica, whence it is termed collectively Salonica opium. The opium districts in Bulgaria are Küstendil, Lowtscha, and Halitz. The produce is mostly consumed by local pharmacy; but, while the country remained under Turkish dominion, any surplus found its way to Constantinople.

The market at Smyrna receives the products of Afium Karahissar, Ushak, Akhissar, Tanshauli, Isbarta, Koniyeh, Bulladan, Hamid, Magnesia, and that collected in the neighbourhood which is known as Yerli. For a description of the physical characters of the numerous varieties of Turkey opium *v.* E. M. Holmes (Ency. Brit. 9th ed. 17, 789).

In the English market Turkey opium is divided into three classes, known as 'shipping,' 'druggists',' and 'manufacturing' opium. As *shipping* opium are classed those varieties which contain the least proportion insoluble in water, and which yield the greatest quantity of extract adapted for smoking. These are the opiums of Malatia, Tokat, Salonica, Balukhissar, Kurkagatsch, Bokaditz, and 'prime' Angora and Yerli. This opium is exported to China, Peru, the West Indies, British Guiana, Brazil, and for reshipment, to the United States. *Druggists'* opium is selected for a high percentage of morphine and includes the varieties which are used in medicine. It has a firmer consistence and a darker colour than the others. In England the products generally chosen are: Beybazar, Yerli, Karahissar, including Adet, Amasia, Akhissar, and 'current' Smyrna and Angora; for America, Ushak, Yerli, and Karahissar; and for the Continent, Ghéve. *Manufacturers'* opium is used for the preparation of alkaloids and includes 'chiqinti,' Persian, and other low-priced opiums (Holmes).

Among the various adulterants which have been detected, from time to time, in Turkey opium are: sand, clay, grape-juice thickened with flour, fig-paste, liquorice, half-dried apricots, tragacanth, pounded poppy capsules, and even turpentine, stones, and bits of lead.

The opium trade in Constantinople for 1886-7 was: imports 768, exports 906 cases; 1887-8, imports 2,790, exports 2,243 cases (S. C. I. 1889, 654). The opium exports of Smyrna for 1888 were 3,128 cases; of these 1,459 cases went to America, 719 cases to England, 239 to France, and the remainder to Austria, Germany, and other countries (Chem. a. Drug. 1890, 36, 12). Production of opium in the Turkish Empire during the last twenty-six years (S.C.I. 1890, 338). The total opium trade of the United Kingdom, which is confined almost entirely to Turkey and Persian opium, for the years 1885–8 was in lbs.:—1885, imports 710,099, exports 425,196; 1886, imports 521,124, exports 368,107; 1887, imports 654,122, exports 353,137; 1888, imports 587,365, exports 535,397 (S. C. I. 1889, 486).

Egypt. Only a small quantity of opium is now exported from Egypt. In 1872 9,636lbs. reached the English market. Owing to its inferior quality it is not regularly imported. Small consignments are, however, sent to Turkey and other countries on the Mediterranean sea-board. It is cultivated in Upper Egypt near Esneh, Kenneh, and Assiout, the ancient Thebaïd. Allen, in 1861, describes the collection of opium from a white poppy. The capsules are slit twice transversely, and the juice collected the following day with a sort of scoop-knife, and placed on a leaf, in the sun, to harden (Ph. [2] 4, 199). The product is sent out in cakes, enveloped in poppy leaves, but without Rumex fruits. According to information supplied to Martindale, the best opium is collected at Akmim, on the right bank of the Nile, 320 miles above Cairo; while at Assiout, 250 miles above, an inferior quality is produced. A piece of Akmim opium, in the form of a hard flat cake, four inches in diameter, and one inch in thickness, contained 7·24 p.c. of morphine. There was the mark of a leaf adhering to it, and it had a rough and irregular appearance. A specimen from Assiout, consisting of segments of a cake, much softer and evidently adulterated, yielded only 0·6 p.c. of morphine (Ph. [3] 19, 743). Other specimens have given 5·8 to 12·2 p.c. (Guibourt, J. 1862, 374), 3·4 to 3·9 p.c. (Petermann, J. 1866, 704), and 5·8 p.c., together with 8·7 p.c. of narcotine (Fl. a. H.). It has also been shown by Gastinel that opium can be made in Egypt containing 11 to 12 p.c. of morphine. The fact that it generally contains only half that proportion is due partly to an over-moist soil and unskilful collection, but also doubtless to adulteration (Fl. a. H.).

Persia. The quantity of opium produced in Persia has until recent years been small and inferior in quality. The strongest, the *Teriak-e-Arabistani*, was obtained from Dizful and Shuster, in Khuzistan. A good quality was produced near Sari and Balfarush, in Mazandaran, near the Caspian, and in the southern province of

Kerman. Inferior sorts came from Shahabdulazim, Kashan, and Kum. The cultivation extends into Turkestan, where a sort of meconium is also manufactured. Part of these products went overland to China, by way of Bokhara, Khokan, and Kashgar, and another part found its way to Constantinople, by way of Trebizond, to be sold as Turkey opium (Fl. a. H.). More attention is, however, now given to the cultivation of the plant and the collection of the juice, and there is less adulteration, the result being a great increase in the trade. The poppy cultivated is the variety *album* (Boissier), having roundish ovate capsules. Shiraz and Behbahan, the latter in the neighbourhood of Bushire, and other new districts, furnish supplies (Ph. [3] 11, 804), and old centres like Kum, Teheran, and Yezd, have improved the quality of their product (Ph. [3] 15, 113 a. 430). More recently Ispahan has become the chief centre of the opium cultivation, the other important districts now being Shiraz, Yezd, Khonsar, and also Khorasan, Kermanshah, and Fars.

The Persian exports of opium in 1859 were estimated at 300 chests, but in 1870 they had risen to 2,600 chests. At that time a regular trade by water was established from the ports cf Bushire and Bunder Abbas, in the Persian Gulf, and the quantity exported increased rapidly. By far the greater part is now shipped from these ports direct to Hong Kong, where it competes in the market with the product of Patna, Benares, and Malwa. A smaller part is shipped to the Straits Settlements, and the rest to England. A less important trade continues with Constantinople, by way of Trebizond and Samsun, and part of the opium made in Teheran, Tabriz, and Kermanshah, also finds its way to Smyrna. Opium is now the chief export of Persia—4,512 chests were shipped in 1882 from Bushire, and 2,000 chests from Bunder Abbas. Of these 1,000 chests came to London, and the remainder went to Hong Kong (Ph. [3] 14, 510 ; *cf.* Fl. a. H. ; Holmes).

According to recent reports the yearly crop of opium in 1887 in the neighbourhood of Ispahan was estimated at 519,680 lbs. The cultivation of the poppy has seriously encroached on the land devoted to corn and other cereals. Indeed, the production of opium engages the energies of the greater part of the population in that district. The capsules are ready for cutting at the beginning of June. Vertical incisions are made, and the juice is collected and conveyed to the market in copper vessels. There it is manipulated to suit the tastes of buyers in Hong Kong and London, whither it is exported between September and January. One of the most celebrated products is that of the village of Kupa, a short distance east of Ispahan. Some of the Ispahan opium is not shipped directly, but is sent to Shiraz or Yezd, where it is first mixed with the products of those districts (Ph. [3] 17, 904).

Persian opium appears in various forms of flat rounded cones or cakes, weighing from 6 to 10 oz. or more, and also in sticks. The cakes are packed in poppy 'trash,' or wrapped in paper or sometimes in poppy, fig, or vine leaves. The drug is usually much finer and smoother than Turkey opium. Its colour is chocolate brown, and it has the appearance of having been beaten into a uniform mass previous to its being made into lumps (Holmes). Under the microscope it is highly crystalline, and when seen with polarised light shows a variety of beautiful forms. Except in the case of specimens collected with the use of oil the odour is nearly the same as that of the Turkish drug. It sometimes contains as much as 13 to 30 p.c. of glucose. Good Persian opium yields when dried 8 to 10 p.c. of morphine, while inferior qualities contain only 3 to 0·5 p.c., or even as little as 0·2 p.c. (Fl. a. H.). Séput found 10·08, 10·12, 11·52, and 13·47 p.c. (J. Ph. [3] 39, 163) ; Guibourt, 11·4 p.c. (J. 1862, 374).

India. Opium is one of the most important products of India. It is a State monopoly of the Bengal Government in Behar and Benares, and is cultivated free in the Malwa and other districts of the native States, whence on arrival in British territory it pays duty. The largest net revenue obtained by the Indian Government was in 1880–81, when it reached a total of Rx.9,262,236. Of this the trade with China and the Straits yielded Rx.8,451,273, the remainder, Rx.810,963, being derived from opium consumed in India. In 1889-90 the export revenue had declined to Rx.6,979,394, home consumption yielded Rx.928,928, giving a total of Rx.7,908,322 (Watt, Parliamentary Return, E. I. Opium, 1891). With the exception of an occasional specimen of Malwa opium, the Indian drug is never seen in English markets.

The area devoted to poppy cultivation in Bengal comprises the large central tract of the Ganges, about six hundred miles in length and two hundred in breadth. It extends east and west, from Dinajpur to Agra, and north and south, from Gorakhpur to Hazaribagh. According to Watt the average annual area actually occupied by the poppy in Bengal for the last thirty years has been 490,000 acres. The State does not restrict the cultivation of opium ; but it is a monopoly in the sense that what is cultivated must be sold to the Government at a price agreed upon beforehand. One object of these regulations is to prevent the neglect of cereals, for the poppy culture is very much more profitable ; in Malwa it is said to realise from three to seven times as much as the ordinary crops. The opium of Behar and Benares is sold at auction in Calcutta, part is retained for consumption in India, but the greater portion is shipped to China. In the year 1889–90 there were exported from Calcutta 57,000 chests, and 4,949 chests were issued to the Excise for use in India.

The remainder of the opium raised in India is produced by the native States. The most important centre is the broad tableland of the Malwa and the adjoining slopes of the Vindhya Hills. The opening of the railway has given a great impetus to the cultivation in Rajputana and Malwa (Ph. [3] 15, 207). Smaller but increasing quantities are produced in the Punjab, not only in the plains, but to the eastward of Lahore, in the valley of Bias, as high as 7,500 feet above the sea. Kulu also produces excellent opium. It is raised in Nepal, Basahir, and Rampur, and at Doda Kashtwar, at the base of the Himalayas, in the Jammu territory, from which districts it is sent to China overland

(Fl. a. H.). Nearly all the opium produced in the native States, however, enters British territory, and pays a duty according as it comes from the districts of Ahmedabad, Ajmere, or Malwa. It is then sent to Bombay, whence, under the general name of Malwa opium, it is shipped to China. In the year 1889-90 Bombay exported 29,029 chests.

The poppy grown in India is the same variety as that of Persia. The same requirements of soil and climate have to be met. In addition to the dangers to which the crop is exposed in Asia Minor the plant in India is liable to the attack of a parasitical species of broom rape, *Orobanche indica*, which attaches itself to the roots and causes the plant to wither. The factory for the Behar district is at Patna, and for the Benares district at Ghazipur, where the Government agents are stationed. In Benares and Behar the seed is sown in November, and the capsules are ready in February or March. They are then incised or scarified vertically, by means of an instrument, constructed of several blades bound together, called a 'nushtur' (*cf.* plate, Ph. [1] 11, 207). This operation is repeated, in the course of a few days, on different sides, each capsule being scarified from two to six times. The next morning the juice, which has exuded, is scraped off by the use of a sort of concave trowel made of sheet iron, called a 'seetoah,' and collected in earthen pots. The poppy capsules are afterwards utilised in a variety of ways and the oil expressed from the seeds. In Malwa the capsules are ready in March or April. A somewhat different instrument is used to collect the juice, and from time to time this is dipped in linseed oil to prevent the juice adhering. Owing to the heavy dews the juice in India is much more moist than in Asia Minor (Ph. [1] 11, 209).

When freshly collected the juice consists of a wet granular mass of a pinkish colour, from which there collects in the bottom of the vessel a dark coffee-coloured acid liquid 'pasewa' or 'pussewah.' More of this liquid is separated by draining, and the opium is then carefully dried by exposure to the air, but protected from the rays of the sun. The drying is continued some three or four weeks until the moisture is reduced to 30 p.c., the amount allowed by the Bengal regulations. In this state it arrives at the Government factory, where it is examined physically and chemically, and if satisfactory is admitted. In the factory great care is taken, by mixing low and high quality opiums, to send out a uniform product. It is manipulated into balls, and covered with poppy petals, which have been carefully dried previously. The petals are made to adhere together into a sort of shell by means of a liquid called 'lewa' or 'lewah,' made partly of opium and partly of 'pasewa.' The spherical cakes, which have a diameter of about six inches, and are not unlike in appearance a 24 lb. shot, are rolled in poppy 'trash,' powdered stalks, capsules, and leaves, put into earthenware moulds and exposed to the sun. If blisters form, the cake shells are opened, the gas allowed to escape, and then tightly closed again. After three days, about the end of July, the cakes are put into frames and exposed to the air. There they remain, with constant watching, until October, when they are packed in chests, which contain wooden compartments for 40 cakes, and the interstices are loosely filled with poppy 'trash.' The chests, which contain 160 lbs., are then ready for exportation to China (Eatwell).

That which is consumed in India, 'abkari' opium, is prepared somewhat differently. It is dried by exposure to the sun until it contains only 10 p.c. of moisture, in which condition it admits of being moulded like wax. It is made into square bricks about 2 lbs. in weight, wrapped in oiled paper and packed in boxes furnished with suitable compartments. Except that the aroma is not quite so good, 'abkari' opium is equal in quality to that prepared for China (Eatwell, Ph. [1] 11, 269, 306 *a*, 359).

The opium of Malwa and other native districts is not so uniform in quality as that of the Government factories. Malwa opium contains only about 5 p.c. of moisture, and it is sent out in bricks or rounded masses which are not incased in poppy petals.

The percentage of morphine in Indian opium is much less than that found in the opium of Asia Minor. It is remarkable that a superior product in this respect has not been obtained to supply the English market, especially in view of the decreasing trade between India and China. Benares opium in 1845-9 contained 2·2 to 3·2 p.c. of morphine (Eatwell). Specimens of Patna garden opium, prepared especially for medicine, yielded 8·6 p.c. (Fl. a. H.), 7·7 p.c. (Guibourt), 9·5 p.c. of hydrochloride (Christison). Specimens from the India Museum gave the following percentages of morphine: 'Khandesh,' 6·1 p.c.; 'medical opium,' 1852-3, part of a brick, 4·3 p.c.; 'garden Behar,' 4·6 p.c.; 'Abkari provision,' 'Patna,' 3·5 p.c.; 'Sind,' 3·8 p.c.; 'Hyderabad,' 3·2 p.c.; and 'Malwa,' 6·1 p.c. (Fl. a. H.). Three specimens of Malwa opium examined by W. D. Howard contained 4·8 p.c., 6·0 p.c., and 9 p.c. of morphine (Fl. a. H.).

Small quantities of morphine salts sometimes reach this country from India. They are made at the Government laboratories at Ghazipur from opium which has been confiscated on account of adulteration, and are not likely to become an important article of commerce (S. C. I. 1889, 917).

China. The Chinese consume nine-tenths of the opium exported from India, all their own production, and part of that of Asia Minor and Persia. It is not possible to estimate the amount produced in China, but some idea of the enormous increase during recent years may be gathered from consular and other reports. The various attempts of the Chinese Government to prohibit the manufacture of opium have had little effect. It was about 1830 that it began to be produced in notable quantities. In 1869, in a Report on the Trade of Hankow, addressed to the inspector-general of customs at Peking, the annual yield of the three provinces Yunnan, Kweichow, and Szechuen, was estimated at 41,000 peculs. In the same year it was reported that two-thirds of Szechuen and one-third of Yunnan was devoted to the poppy (Calcutta Blue Book, 205). In 1882 the annual production in the south-west of China, chiefly the provinces of Szechuen and Yunnan, was estimated at over 200,000 peculs, or more than twice the whole importation from India (Ph.

[3] 13, 225; *cf.* S. C. I. 1890, 74). In 1885 the imports of Indian opium in Manchuria had fallen to only 5 p.c. of what they were in 1866, its place being taken entirely by the native drug (Ph. [3] 18, 280). In 1887 the district of Wenchow was occupied almost entirely in the production of opium. The country, viewed from a hill-top, was, in many places, one vast brilliant mass of poppy, with here and there a patch of green (S. C. I. 1888, 409). The consul at Niew Chang, in Manchuria, reports in 1889 that, although twenty years before 2,635 peculs of Indian opium supplied the whole province, at that time the port of Yingtzu alone consumed 3,744 peculs annually. This enormous demand was being met almost entirely by the native drug. The use of Indian opium has decreased so much that in a few years' time it will only be known to wealthy connoisseurs (S. C. I. 1889, 653). A similar report comes from Chin Kiang (S. C. I. 1889, 931). Importation of Turkey opium (S. C. I. 1890, 775).

Opium is cultivated chiefly in Szechuen, Yunnan, and Kweichow, to a less extent in Shanse, Shense, and Shantung, also in eastern Mongolia, and in Manchuria. The development of the poppy cultivation has been so great in many parts of China that it has seriously interfered with the supply of cereals. For this reason, since the famine, it has been prohibited in Shense, Honan, and Chihli. In Kwangtung the soil and climate are not suitable, and in Fuhkeen the production of sugar is equally or more remunerative (Holmes). In Szechuen the poppy is a winter crop, and may be gathered in time to allow rice to be planted, and thus not interfere with the summer produce. The yield of opium is about 22 lbs. to the acre. Every part of the plant has a use, if only for manure, and thus the total return amounts to about double that of cereals. As soon as the summer crop is reaped, the soil is prepared and manured with night-soil. The seeds are sown in December, in drills $1\frac{1}{2}$ foot apart, the white poppy being the most commonly cultivated in the low grounds. After a month, when the plants are a few inches high, the rows are thinned and banked up with earth. In March or April the flowering takes place, and at this time the roots are again well manured with night-soil. The capsules are slit in April or May (Ph. [3] 13, 225). According to Thorel, the scarification and collection is precisely the same as that carried on in India. Some Szechuen specimens seem to have been collected with the use of oil as in Malwa (Fl. a. H.).

Yunnan and Szechuen opium is made into flat cakes and wrapped in white paper. It is darker and softer than that of Persia, which it resembles. Chekeang is a treacly extract sold in 2 to 4 lb. jars. The product of Shense was supposed to resemble in flavour the highly-prized Patna opium. Yunnan ranks next and then Szechuen (Holmes). A specimen of Chinese opium, examined by Jamieson, contained:—Moisture, 18 p.c.; morphine, 5·9 p.c. (or 7·2 p.c. in dried drug); narcotine, 7·5 p.c.; ash, 7·5 p.c. (Report on Trade of Hankow). Authentic specimens examined by Sheppard gave the following percentages of morphine in the dried opium:—Szechuen, 2·2; Kweichow, 2·5; Yunnan, 4·1; Kansu, 5·1. Eatwell in Szechuen found 3·3 and in Kweichow 6·1. Sheppard found 5 to 14 p.c. of moisture and 36 to 53 p.c. of extract soluble in water (Fl. a. H.).

Mozambique and Algeria. In 1877 a Portuguese company was founded to commence the opium culture in Mozambique (Ph. [3] 8, 1007; 10, 63, 13, 445). In 1882, according to Guyot, some three hundred labourers were employed in cultivating Zambesi opium between the Muto and Quaqua rivers. The yield compares favourably with that in India. The product is said to be largely admixed with foreign substances before being made into 500 gram balls, which are packed in boxes containing poppy 'trash,' and covered with indigenous cotton (C. R. 95, 798). These balls are sometimes seen in the English market. According to recent advices, the company has been obliged to go into liquidation, and the cultivation has been abandoned (Ph. [3] 21, 87). Opium has been collected in Algeria in small quantity since 1828 (Ph. [1] 15, 348). A dried specimen examined by Guibourt contained 12·1 p.c. of morphine (J. 1862, 374; Aubergier found 1·5 to 17·8 p.c. (A. Ch. [3] 20, 303).

Australia.—The production of opium commenced about 1868, and the first specimen reached this country from Victoria, and was examined by Morson in 1869. It contained, according to Hood, 2 p.c. of morphine and 8 p.c. of narcotine (Ph. [3] 1, 272). Specimens containing 4·2 to 7·1 p.c. of morphine were sent to England in 1870. They were produced in the village of Sunbury, near Melbourne (Hood). About this time the cultivation was commenced in Gippsland, and opium containing 9 p.c. of morphine, 4 p.c. of narcotine, and 6 p.c. of meconic acid, was obtained (Ward, Ph. [3] 1, 543). The Toowoomba district in Queensland also furnished some good specimens (Ph. [3] 1, 972).

According to later reports, November 1887, the chief part of colonial opium in the Melbourne market comes from the Bacchus Marsh district, where the cultivation had been carried on for some eighteen to twenty years. The sowing takes place at three periods, about the first week in May, the second or third week in June, and the latter part of July. By this means parts of the crop mature in succession. The average yield is 15 to 25 lbs. to the acre, but in a good season as much as 30 to 40 lbs. are obtained. In Europe the average yield to the acre is 25 lbs., and in India 30 to 40 lbs. When the capsules are ready, two incisions are made horizontally, half-way round, and the juice which exudes is collected the next morning. A few days later other incisions are made, until the capsule is exhausted. The opium is manipulated into balls and carefully dried. In quality it approximates to the product of Asia Minor. A recent specimen gave 11·5 of morphine from the dry drug. Another from Queensland contained 9·8 p.c. (Matthews, Austral. J. Pharm. Nov. 1887).

Europe and North America. Attempts have been made in most European countries, in Greece, Italy, Spain, France, Switzerland, Germany, England, and Sweden, to cultivate opium, and the results have shown that, providing the soil selected is suitable, and the rainfall not excessive, it is possible, in all these countries, to produce opium equal to that of Asia Minor. The most important European experiments have been conducted in France. A product called ‘affium’ has been made at Clermont-Ferrand, which is said to contain uniformly 10 p.c. of morphine; but it has not become an important article of trade (Fl. a. H.; Aubergier, Ph. [3] 15, 693). Some interesting investigations have been made in the neighbourhood of Amiens, where specimens of dry opium were produced containing 16 and 20 and still higher percentages of morphine. It was observed by Descharme that the morphine diminished when the juice was slowly dried, and the peculiar odour of the drug is ascribed to a species of fermentation (J. Ph. [4] 6, 222). Guibourt found the percentage of morphine in French opium to vary from 12·1 to 22·8, the latter being the highest proportion of morphine ever recorded (J. Ph. [3] 41, 184 a. 201). Other analyses of French opium give 17·6 p.c. (Descharme, C. R. 40, 34); 17·5 (Chevallier, Fl. a. H.); 8·2 (Roux, J. 1855, 717); 11·1 to 11·9 (Petermann, J. 1866, 704). German opium from Erfurt contained 16·6 and 20 p.c. (Biltz, Gm. 16, 415); from Wurtemberg, 12 to 15 p.c. (Hesse, Fl. a. H.); and from Silesia, 9 to 10 p.c. (Hesse).

Experiments in North America lead to the same results as in Europe. Specimens from Vermont contained 15·75 p.c. of morphine (Procter, Am. J. Pharm. [3] 18, 124); from Illinois, 8·75 p.c. (Kennedy, Am. J. Pharm. [4] 1, 6); and from California, 7·75 p.c. (Maisch, Am. J. Pharm. [4] 3, 103).

Chemical constituents. The important chemical constituents of opium may be divided into alkaloids, neutral compounds, and acids. For full particulars of all of these see under their respective headings, also VEGETO-ALKALOIDS. There are in opium nineteen, or perhaps twenty, alkaloids:—(1) *Morphine*, $C_{17}H_{19}NO_3,H_2O$ or $C_{17}H_{17}NO(OH)_2,H_2O$ the most important constituent of opium. Its discovery and the proportion in which it occurs in opium have been already given. It is crystalline and forms crystalline salts. (2) *Codeine*, morphine methyl ether, $C_{18}H_{21}NO_3,H_2O$ or $C_{17}H_{17}NO.OH.OMe$, was discovered in opium by Robiquet (A. 5, 106) and may be prepared by the action of methyl iodide on morphine. It melts at 155°. Percentage in Smyrna, French, or Indian opium, 0·2 to 0·4 (Ph. [2] 7, 183). (3) *Hydrocotarnine* $(C_{12}H_{15}NO_3)_2H_2O$ occurs in small proportion in opium (Hesse, A. Suppl. 8, 326) and is formed by the oxidation of narcotine (Beckett a. Wright, C. J. 28, 577). (4) *Thebaïne*, $C_{19}H_{21}NO_3$ or $C_{17}H_{15}NO(OMe)_2$ was isolated by Thiboumèry (Pelletier, J. Ph. [2] 21, 569). Turkey opium contains about 1 p.c. (5) *Pseudomorphine* $C_{34}H_{36}N_2O_6,3H_2O$ (Pelletier a. Thiboumèry, J. Ph. [2] 21, 575) occurs in opium to the extent of 0·02 p.c. or even less. (6) *Codamine*, $C_{20}H_{25}NO_4$; (7) *Laudanine*, $C_{20}H_{25}NO_4$; (8) *Laudanosine*, $C_{21}H_{27}NO_4$, and (9) *Meconidine*, $C_{21}H_{23}NO_4$, which exist in opium in minute quantities, were discovered by Hesse (A. 153, 47 a. 56; Suppl. 8, 272, 280 a. 321). (10) *Papaverine*, $C_{20}H_{21}NO_4$, or $C_9NH_4(OMe)_2.CH_2.C_6H_3(OMe)_2$ (Goldschmidt, M. 6, 667) was discovered by Merck in opium (A. 66, 125; 73, 50). It exists to the extent of about 1 p.c. (11) *Lanthopine*, $C_{23}H_{25}NO_4$ (Hesse, A. 153, 57; Suppl. 8, 271). (12) *Protopine* $C_{20}H_{19}NO_5$ (Hesse, A. Suppl. 8, 318) and (13) *Cryptopine*, $C_{21}H_{23}NO_5$ (T. a. H. Smith, Ph. [2] 8, 595 a. 716) are found in opium in very small proportions. (14) *Narcotine*, $C_{22}H_{23}NO_7$. The discovery of this base has been already referred to. It exists free in opium and may be extracted by benzene in which morphine is insoluble. Turkey opium usually contains 1 to 2 p.c. but East Indian and Persian opium often contain much more narcotine than morphine. In some specimens the proportion reaches 10 p.c. It is crystalline, melts at 176° and forms salts with difficulty. (15) *Rhœadine*, $C_{21}H_{21}NO_6$, a base found in the *Papaver Rhœas* (Linn.), probably occurs in opium in minute quantity (Hesse, A. 140, 145). (16) *Oxynarcotine*, $C_{22}H_{23}NO_8$ (Beckett a. Wright, C. J. 29, 461). (17) *Narceïne*, $C_{23}H_{29}NO_9,2H_2O$, was discovered by Pelletier in opium in which it is found to the extent of 0·02 to 0·1 or even 0·7 p.c. (A. Ch. [2] 1, 262). It consists of long colourless prisms which lose water at 100° and melt at 145° with formation of a new base (Hesse, B. 7, 105). (18) *Gnoscopine* $C_{34}H_{36}N_2O_{11}$ (T. a. H. Smith, Ph. [3] 9, 82). (19) *Tritopine*, $C_{42}H_{54}N_2O_7$ (Kauder, Ar. Ph. 228, 419). (20) *Papaverosine*, a base found in poppy capsules by Deschamps (J. 1864, 446) but not hitherto detected in opium. With the exception of morphine and narcotine the remaining bases do not occur in opium to a greater extent together than 2 p.c. and generally not more than 1 p.c.

The neutral compounds are:—(1) *Meconin*, $C_{10}H_{10}O_4$ discovered by Dublanc (A. Ch. [2] 49, 5) but more completely studied by Couerbe (A. 5, 180). It may be obtained by the oxidation of narcotine (Anderson, A. 86, 191; 98, 44) and is formed in other reactions. It is an inner anhydride $C_6H_2(OMe)_2.\underbrace{CH_2.COO}$ (Hessert, B. 11, 257). (2) *Meconiosin*, $C_8H_{10}O_2$ or perhaps $C_6H_2(Me)_2(OH)_2$. It is crystalline, melts at 88°, and was found by T. a. H. Smith in the mother-liquor from the preparation of meconin (Ph. [3] 8, 981).

The discovery of *Meconic acid* $C_7H_4O_7,3H_2O$ has already been mentioned. It is a tribasic acid forming primary, secondary, and tertiary salts. Heated to 100° it loses its water of crystallisation, and at 120° to 200° it breaks up into carbon dioxide and *comenic acid* $C_6H_4O_5$, and at a higher temperature into another molecule of carbon dioxide and *pyromeconic acid*, $C_5H_4O_3$. Meconic acid occurs in opium to the extent of 3 to 5 p.c. in combination with morphine, and perhaps with other bases. The ‘thebolactic acid’ of T. a. H. Smith (Ph. [2] 7, 50) has been shown by Stenhouse (Watts' Dict. 1st ed. 5, 759) and Buchanan (B. 3, 182) to be identical with lactic acid. Turkey opium contains, according to T. a. H. Smith, 2 p.c., but it is probably not an original constituent of the poppy-juice (Fl. a. H.).

The less important constituents of opium represent three-fourths of its weight. *Water* exists to a very variable extent. Turkey opium contains on an average 12·5 p.c. The Bengal opium sent to China is made to contain uniformly 30 p.c. About 50 p.c. of opium is composed of a *gum*, having properties distinct from gum arabic, *pectin*, *albumen*, and fragments of capsules. *Sugar* is present in French opium to the extent of 6·5 to 8·0 p.c., and is said to be uncrystallisable. Of that part of Turkey opium insoluble in water, 6 to 10 p.c. is composed of *wax*, pectin, and insoluble calcium salts. The wax, which exists in the juice as an emulsion, is a mixture of *cerotyl palmitate*, and *cerotyl cerotate* (Hesse, B. 3, 637). Vermont opium contained 11 p.c. of *caoutchouc* (Procter). The *colouring matter* and a *pungent volatile substance*, which is removed by benzene or acetone, have not been examined. Opium leaves 4 to 8 p.c. of *ash* consisting chiefly of sulphate and phosphate of calcium and magnesium. Poppy-juice contains no starch or tannin. The presence of these substances in opium is therefore an indication of adulteration.

Microscopic examination of opium and the constituents extracted by solvents (Deane a. Brady, Ph. [2] 6, 234; 7, 183). Analyses of opium by Mulder, Schindler, Biltz (Pereira, Mat. Med. 1853, 2, 2097). Examples of recent analyses: Persian opium (W. D. Howard, Ph. [3] 6, 721); Australian opium (Ward, Ph. [3] 1, 543; Matthews, Austral. J. Pharm., Nov. 1887); Vermont opium (Procter, Am. J. Pharm. [3] 18, 124); Flückiger (J. 1869, 797; Ph. [2] 10, 208).

Physiological action and uses.—Opium is without doubt the most important remedy available for use in medicine. Its action on man is chiefly on the brain, producing sleep. In doses of a grain or less, a stage of slight excitement supervenes during which the individual can control his energies. In 1 to 2 grain doses the stage of excitement is short and is succeeded by deep sleep, after which there is nausea and headache. If large doses of 3 grains or more be administered the excitement is very short and is followed by sleep which becomes more and more comatose until the patient cannot be aroused. If death takes place the respiration ceases first. Opium is used for the alleviation of pain, either generally or locally, for the production of sleep, or for reducing the irritation of various organs. Its special applications in the treatment of disease are almost endless (*cf.* Brunton, Pharm. Therapeut., 1887, 852).

The action of opium in stimulating and then depressing gives rise to the desire to repeat the dose. In this way the habit of 'opium eating' is contracted. The worst effects of opium are thus obtained. It deranges the nervous system, and impairs the intellectual and moral and finally also the physical powers. De Quincey's description of his own experience is well known.

But by far the largest quantity of opium is used for smoking. The habit is believed to have originated in Persia, but it is in China where it prevails to the greatest extent at the present day, where, indeed, its use appears to be almost as widely diffused as the use of tobacco in Europe. For smoking the opium undergoes a process of preparation which is a business in itself. In Hong Kong, according to McCallum, the opium is extracted by boiling with water and the clear solution is evaporated until it attains the consistence of treacle (Ph. [3] 11, 229; 12, 446). The Chinese in California first put the opium through a series of roasting processes which are said to destroy its stickiness and render it more easily extracted by boiling with water (Calvert, Ph. [3] 120, 148). The Chinese recognise four varieties of opium:—(1) Raw opium; (2) Prepared opium, the treacly extract described; (3) Opium 'dross,' the scrapings of the opium pipe, which are said to be strong, hot, of inferior flavour; (4) Opium 'dirt,' the exhausted marc after extraction with water (McCallum).

The whole operation of opium-smoking is described in a letter which accompanied an opium-smoker's set of apparatus in 1882 from Canton to Kew. The pipe has a flat bowl made of metal with a very small opening. A drop of the soft opium is taken on the point of a 'dipper' and dexterously roasted in the flame of a little lamp until with constant burning it has the appearance of burnt worsted. Then, first warming the bowl of the pipe, the drug, about the size of a hemp-seed, is placed about the opening in the bowl, the pipe taken in the mouth and the opium ignited. The smoke is partly swallowed or inhaled and partly exhaled by the mouth and nose. The preparation for smoking occupies 5 or 10 minutes, but the actual smoking only about 30 seconds (Sampson, Ph. [3] 11, 22).

The physiological action of opium smoked in this way is clearly quite different from what it is when taken in the stomach. It is noteworthy that those opiums most highly prized for smoking contain a small percentage of morphine. It would seem that, notwithstanding the serious view of the effects of opium-smoking taken by the Chinese Government and held by many Europeans, the habit is not more injurious than the use of other stimulants. Opium in the East seems to perform the same function that alcohol does in the West, and, as far as can be ascertained, with about the same good and bad effects (*cf.* Birdwood, Ph. [3] 12, 500; Spence, Ph. [3] 13, 226; McCallum, Ph. [3] 14, 27; James, Ph. [3] 18, 280). A. S.

OPOBALSAM *v.* Oleo-resins.

OPODELDOC. *Linimentum Saponato-camphoratum.* A solution of soap, camphor, and volatile oils in alcohol, used externally in rheumatism, sprains, &c.

OPOPANAX or **OPOPONAX** *v.* Gum-resins.

ORANGE, CHROME, *v.* Chromium.

ORANGE, CROCEÏN *v.* Azo- colouring matters.

ORANGE, GOLD *v.* Azo- colouring matters.

ORANGE M *v.* Azo- colouring matters.

ORANGE, MANDARIN, *v.* Azo- colouring matters.

ORANGE, METHYL, *v.* Azo- colouring matters.

ORANGE, NAPHTHOL, *v.* Azo- colouring matters.

ORANGE OCHRE. *Burnt Roman ochre* *v.* Pigments.

ORANGE OIL *v.* Oils, essential.

ORANGE, PALATINE, *v.* Palatine orange.

ORANGE RUSSET. *Rubens madder* *v.* Pigments.

ORANGE, SALICYLIC, *v.* Salicylic yellow.

ORANGE YELLOW *v.* Azo- colouring matters.

ORAOGEITE *v.* Thorium.

ORCEÏN *v. Orcinol*, art. Phenol and its homologues.

ORCHELLA WEED *v.* Archil.

ORCHIL *v.* Archil.

ORCHIL SUBSTITUTE *v.* Azo- colouring matters.

ORCIN *v. Orcinol*, art. Phenol and its homologues.

ORCINOL *v.* Phenol and its homologues.

ORCINOL PHTHALEIN *v.* Phthaleïns.

ORDEAL BEAN. *Calabar Bean, Physostigma, Eseré Nut*; *Fève de Calabar*, Fr.; *Kalabarbohne*, Ger. The seeds of the *Physostigma venenosum* (Balfour, T. E. 22, 305), a climbing plant, inhabiting the banks of the Niger and Old Calabar rivers near their mouths, in Western Africa (*cf.* Bentl. a. T. 80, and, for an allied species, Holmes, Ph. [3] 9, 912). The plant has a woody stem, and ascends to a height of fifty feet. The seeds are exceedingly poisonous, a property known to the natives in the neighbourhood of the Gulf of Guinea, by whom they are administered as an ordeal to be undergone in cases of suspected witchcraft. Daniel, about 1840, introduced ordeal bean into Europe (N. Ed. P. J. 40, 313), and its physiological action was examined by Christison (Ph. 14, 470). It causes a marked contraction of the pupil of the eye, and on this account is much used in ophthalmic medicine. With regard to the antagonism between ordeal bean and belladonna, *v.* Bennett (Brit. Med. J. 1875, 464). It is given in cases of poisoning by strychnine, and generally in tetanus and chorea (*cf.* Fl. a. H. 191).

The physiological activity of ordeal bean depends chiefly upon the presence of the alkaloid *physostigmine* $C_{15}H_{21}N_3O_2$, discovered by Jobst and Hesse (A. 129, 115). The 'eserine' of Vée and Leven (J. Ph. [4] 1, 70) is doubtless the same compound. To obtain it the seed is exhausted with alcohol, and the alcohol removed from the solution by distillation. The residue is mixed with sodium bicarbonate and extracted with ether. The ethereal solution is shaken with water containing sulphuric acid, and the acid solution of alkaloidal sulphate is treated with excess of sodium bicarbonate. Ether now extracts the physostigmine and yields it as a brittle varnish on evaporation (Hesse, A. 139, 82). Petit shakes the last ethereal solution with water, containing just sufficient sulphuric acid to neutralise the alkaloid. In this way, after removal of the ether and evaporation, crystals are obtained of neutral sulphate of physostigmine (J. Ph. [4] 14, 255).

Physostigmine is tasteless but exceedingly poisonous. It forms colourless or pinkish crystals which melt at 45°. It is soluble in alcohol, ether, benzene, carbon disulphide, and chloroform; but is only sparingly soluble in water. It oxidises readily, especially when moist, at 100°, a compound being formed which gives a red colour with acids. Chlorinated lime also gives a red colour reaction with physostigmine. The alkaloid in solution precipitates ferric chloride, and combines with acids to form *salts.* Besides the sulphate, the hydrobromide (Duquesnel, Ph. [3] 5, 847; Ph. [3] 12, 825) and salicylate $C_7H_6O_3$, $C_{15}H_{21}N_3O_2$ (Merck, Ph. [3] 9, 976) have been obtained in crystals. Most alkaloidal reagents precipitate physostigmine. The compound with potassio-mercuric iodide $C_{15}H_{21}N_3O_2,HI,HgI_2$ is white, insoluble in water, but soluble in alcohol, from which it may be obtained in crystals which melt at 70° (Hesse). When the alkaloid is neutralised with dilute sulphuric acid, and an excess of ammonia added, and the mixture evaporated to dryness, a magnificent blue residue remains. The blue compound is soluble in water and alcohol, and may be crystallised from these solvents in elongated prisms. If to a solution of the base in water ammonia be added and the mixture be evaporated at 100° a bluish residue remains, which on the addition of an acid becomes beautifully dichroic blue and red (Petit, C. R. 72, 569; J. C. Umney, Ph. [3] 20, 1061).

According to Harnack and Witkowsky (Ph. [3] 8, 2), ordeal bean contains a second alkaloid, *calabarine*, which differs in its solubilities and its physiological action from physostigmine; indeed, it appears in the latter respect to resemble strychnine. Another compound, *phytosterin* $C_{26}H_{44}O,H_2O$, has been isolated in a definite form by Hesse (A. 192, 175). It would seem to be a homologue of cholesterin. It consists of brilliant tabular crystals, which melt at 132°–133°, and is extracted from the seed by petroleum ether (*cf.* MacEwan, Ph. [3] 17, 641). By acting on physostigmine with reducing agents, Eber (Ph. [3] 19, 161 and 345) has recently obtained a compound *eseridine* $C_{15}H_{23}N_3O_3$, which is said also to be a constituent of the seed. It liberates iodine from hydriodic acid. By treatment with acids it is reconvertible into physostigmine.

For estimation of alkaloids in ordeal bean by means of Mayer's reagent *v.* Masing (Ar. Ph. 1877, 310). Gravimetric methods (Gibson, Ph. [3] 15, 593; MacEwan, Ph. [3] 15, 594; 17, 642). A. S.

OREIDE. An alloy of a brilliant-yellow colour, resembling gold, made by taking copper 100, zinc 17, magnesia 6, sal ammoniac 3·6, lime 1·80, and tartar 9. The copper is melted and the other materials are added in small portions at a time, and the fused mass is skimmed and kept melted for about half an hour. The alloy has a fine grain, is malleable, takes a most brilliant polish, and if it tarnishes its lustre is restored by acidulated water (Ure).

ORELLIN. A yellow colouring matter contained in annatto, which is derived from the fruit capsules of *Bixa Orellana.* Soluble in water and alcohol.

ORICHALCUM. A form of brass in use among the ancient Greeks and Romans.

ORIENTAL EMERALD. The name given to the green sapphire.

ORIENTAL TOPAZ. The name given to the yellow sapphire *v.* Aluminium.

ORIGANUM OIL *v.* Oils, essential.

ORMOLU *v.* Mosaic gold.

ORNITHITE. A tricalcic phosphate $Ca_3P_2O_8.2H_2O$, found in monoclinic crystals in guano; *v.* Calcium.

ORPIMENT. *Arsenic sulphide v.* Arsenic.

ORRIS ROOT is the dried rhizomes of *Iris florentina, I. pallida*, and *I. germanica.* It is characterised by a pleasant aroma, and appears to be slightly detergent and antiseptic. It is employed in the preparation of violet-powder and dentifrices.

ORSEILLINE *v.* Azo- colouring matters.

ORTHITE *v.* Cerium metals.

ORTHOCLASE. *Common potash felspar v.* Felspar.

ORTHOCYMOPHENOL *v.* Phenol and its homologues.

ORTHO-NITRO-PHENYL-PROPIOLIC ACID *v.* Indigo.

OSAZONES. A term given by E. Fischer to compounds of phenyl hydrazine with the sugars (*v.* Hydrazones).

OSMIRIDIUM *v.* Platinum metals.

OSMITOPSIS, OIL OF. *Osmitopsis Asteriscoïdes*, an aromatic plant of the order of *Compositæ*, growing in South Africa, yields a greenish-yellow oil of a burning taste and aromatic smell. Appears to be isomeric with borneol and oil of cajeput.

OSMIUM *v.* Platinum metals.

OSTEOLITE *v.* Calcium.

OTTO or **OTTAR OF ROSES** (*v.* also Attar of roses, vol. i.). The most important centre of the production of otto of rose is in the region of the Balkan Mountains, and includes about 150 villages situated in the two valleys of Toundja and Strema, affluents of the river Maritza. These two valleys run from west to east, and lie between the Great Balkan chain on the north, and the Svedna Gora mountains on the south, the extreme points where rose culture is carried on being Koprivchitza on the west, and Twarditza on the east. The best otto is obtained on the southern slope of the Balkans. Here the climate is temperate, but the variations in temperature are sudden and frequent. The ground is sandy and porous, as a rule; where this is not the case, and water accumulates, roses are killed by the frost or by fungi, which attack the roots. Although the rose cultivation extends over a large tract of country, it is nowhere conducted on a large scale by any one individual, but is divided into a large number of small plots belonging to small proprietors. The dealers live in the towns, and, although they sometimes buy the flowers and distil the oil, they rarely cultivate the roses, and then only to a small extent.

The roses are grown in long borders or plots 100 or 200 mètres long, the plants attaining the height of a man. Between the plots a space of 1½ to 2 mètres is left, so as to allow of a cart passing along between them.

Two roses are usually cultivated, a red and a white one, specimens of which, gathered in the Hejanlik plantations, have been identified by Blondel. The red one proved to be a branching form of *Rosa damascena*, and the white one *Rosa alba.*

The *Rosa alba* is employed to form a dividing line between the different plantations, and is also grown at the end of each plot, so as to present only roses of less value to the peasant, who would otherwise steal the more valuable red rose; it is not used, as a rule, for distillation. Dishonest cultivators, however, take advantage of the fact that when distilled it yields a product rich in stearoptene (although of poor fragrance), to mix it with the red rose, and thus obtain an otto which will bear dilution with Turkish oil of geranium (oil of *Andropogon Schœnanthus*, L.).

In May of the second year the rose trees are about 2 feet high, and yield sufficient flowers to pay the expense of their cultivation up to that date. The next year they are in full bearing, and the maximum product is obtained when they are five years old, although the plants will live more than 20 years. At 10 years of age they are, however, usually cut level with the ground, new branches, and even flowers, appearing the next year. The flowers commence to expand between May 20 and 28, and they are collected daily till June 15 and 20. The collection commences every day at dawn, for an opening flower-bud left till next day will then have lost its fragrance and its colour.

The contents of the basket are weighed in the field, paid for, and emptied into sacks, which are carried at once to the distillery. If the white roses are present in too large proportion they are paid for separately at a lower price. The stills are usually placed in sheds near the river, for the convenience of obtaining a good supply of water, and in some cases are let by the proprietors at the rate of 4 francs per still. The stills are of copper, and are made to contain 75 litres of water and 10 kilos. of flowers. The latter are introduced by means of an osier basket, and the stills are heated with long logs of wood lighted at one end placed under the still. After a time, if steam comes out of the refrigerating tube, the fire is moderated, and when 10 kilos. (two flasks) of rose-water have distilled over, the fire is removed by withdrawing the burning logs. The still is opened, the contents strained through the osier basket, and the water remaining in the stills saved for the next distillation. If the operation is continued until 15 kilos. of rose-water is obtained, the otto is of inferior quality, and contains more stearoptene.

The rose-water is then submitted to distillation a second time, 40 litres being distilled at a time, and only 5 litres collected. The vessels in which it is received have the shape of a long-necked flask, and the water is at first milky, like an emulsion, the oil floating after a time in the neck of the flask. It is removed by inserting a conical tin funnel about two centimètres long, furnished with a slender handle, and having a capillary orifice. It is dipped below the surface of the otto, and when a drop of oil on raising the funnel appears at the orifice it is emptied quickly into a special flask.

About 3,000 kilos. of flowers are calculated to yield a kilo. of otto, and this quantity of flowers is the usual yield per hectare, so that it may be considered that a hectare of roses yields a kilo. of otto. The adulteration of the otto takes place chiefly by the addition of oil of rose geranium (*Andropogon Schœnanthus*), where the congealing point is lowered from 15° or 16° R. to 14°, 13°, or 12°, and even lower. The purchaser of otto generally brings with him a basin and thermometer, and having obtained the desired temperature by mixing warm and cold water, and testing the temperature with the thermometer, inserts a flask containing 15 grms. of the essence to be tested. In about three minutes crystalline needles appear, and in ten minutes the otto is solid enough for the uncorked flask to be reversed without spilling a drop. The price varies according to the degree of congealing-point, that below 12°R. being openly sold at a special rate. The average production of otto of rose in Bulgaria is about 3,000 kilos. in good years, and 1,500 kilos. in bad ones.

The peasants are paid according to the season at the rate of ·32 to ·23 fr. per gramme for otto of standard purity. The flattened circular metal bottles in which it is exported contain 400 grms., 1 kilo., or 2½ kilos., and the price of the pure essence is 800 to 900 fr. per kilo., according to the season. The bottles are generally enveloped in felt. When the essence is freshly distilled it has a slight empyreumatic odour, possibly due to the fact that the water in the stills at the end of the day, having served for several distillations, has dissolved vegetable salts, and boils at a temperature distinctly above the boiling-point of pure distilled water. Otto of rose is also said to be produced in notable quantities in Asia Minor, at Broussa, Bourgas, and elsewhere, by emigrants from Roumelia.

In Provence the cultivation of the rose is at the present time a flourishing industry, and the otto prepared in that district is considered superior to the Bulgarian product; it is obtained from *Rosa centifolia* (a specimen of the plant used from Grasse having been determined by Dr. Blondel). This rose flowers there in April and May. Rose-water is sometimes distilled from the yellowish tea-rose known as *safrano*, which flowers in autumn and winter; but the water is very inferior, and the otto obtained from it is still more so, and unfit to mix with that of *R. centifolia.*

The cultivation of *Rosa centifolia* is carried on chiefly around Grasse, Cannes, Nice, and Valois, by peasant proprietors, who sell the flowers to the distillers in the towns. The chief use of the roses is for making rose pomade, only a small quantity, comparatively speaking, being distilled for the otto. The flowers are distilled in large stills, such as are generally used for spirit, some holding as much as 150 kilos. of flowers. Often one refrigerator receives the condensing pipes of several stills.

Usually 50 kilos. of flowers and 300 litres of water are placed in the still at one time, and 100 litres are distilled over, the first 25 being the richest in oil, and known as *eau double de rose.* The next 30 are of medium and the remaining 45 of inferior quality. The oil which floats is collected by means of a Florentine receiver. The yield of otto is small, 100,000 kilos. of flowers giving only a kilo. of otto, and the price is about 1,000 francs per litre; the average price of the rose-water is 2·60 francs per litre.

In Germany roses have been distilled for about five years in the neighbourhood of Leipzig, about six hectares being at present under cultivation. The species employed is *Rosa centifolia*, and the amount produced in 1887 was 3,000 litres of rose-water and 2 kilos. of otto. The latter congeals at 20°C., and contains 32½ to 34 p.c. of stearoptene, which is in excess of that in Bulgarian otto. Indeed, the proportion of stearoptene present in otto of rose is always greater in cold countries.

Formerly otto of rose used to be adulterated by mixing it direct with oil of ginger grass, but now the flowers are sprinkled with the oil when placed in the retort. The odours under these circumstances amalgamate better, and during the distillation the proportion of waxy (*circuse*) matter that passes over is larger, so that otto thus obtained may solidify at 14°, even when containing 25 p.c. of oil of ginger grass. In this case, however, the otto appears muddy, and does not present the sparkling crystals characteristic of pure otto. The odour also is easily detected by an expert. Bromine turns pure otto of rose of a green colour, but is itself decolourised by oil of ginger grass, and if a few drops of *liquor potassæ* are subsequently added, an apple-green precipitate in viscous clots is formed in a colourless liquid, and the odour of roses is not altered; but if adulterated with ginger-grass oil a yellow milky precipitate is obtained in a reddish liquid, and a disagreeable odour is given off. This test, however, is qualitative rather than quantitative.

The presence of spermaceti or paraffin in otto is detected in Bulgaria by rubbing the small test-bottle of otto, containing about 15 grms., between the hands, when the essence rapidly liquefies, since a temperature of 18°C. suffices, whereas paraffin does not melt until 32°–50° and spermaceti at 46°C., and these remain undissolved at the bottom of the bottle.

Experiments made by Blondel show that pure otto of rose has some physiological effect. In the dose of five, or even of two, drops, it produced cramp of the stomach in the absence of food. Taken after a meal it seemed to stimulate the digestive functions at first, but doses of ten or twelve drops appeared to have an opposite action, and caused marked flatulence. The only general effect noticed was a marked tendency to sleep. A guinea-pig into which a cubic centimètre of otto was subcutaneously injected died in four days after a state of profound torpor lasting forty-eight hours. The only effect noticed in a *post-mortem* examination was a slight congestion of the meninges. In some persons the odour of the rose produces headache, and in rare cases severe symptoms which are probably due to idiosyncrasy. The oil of *Andropogon Schœnanthus*, or Turkish oil of geranium, used to adulterate oil of roses, produces similar symptoms, but in a higher degree.

With regard to the portion of the flower in which the otto is formed, observations made under the microscope indicated that it is secreted by the epidermal cells. Other experiments show that these cells also contain fixed fatty matter, since when the petals are distilled until wholly deprived of odour these epidermal cells are still blackened by osmic acid, and yield to ether a fixed fatty substance. But the fresh petals treated directly with ether, and thus deprived both of fixed oil and essential oil, still show the blackened epidermal cells when treated with osmic acid, but with a bluer tint in them. This is due to tannin, as may be proved on a section of the fresh petal by the use of acetate of iron. When the petals are deprived of their essential oil by distillation, of their tannin by boiling water, and their oil by ether, the epidermal cells no longer become blackened by osmic acid. There is, therefore, every reason to suppose that the chemical changes by which the otto is produced take place in the epidermal cells, or, in other words, that they are not special receptacles of secretion, but secreting cells. The epidermis of the anther does not contain otto, but it is contained in small quantity in that of the filament and on the stigmatic surface and groove, though not in that of the ovary or style (R. Blondel, Les Produits Odorants des Rosières, Paris, 1889, and Pharm. J. 1890, July 5, 3–5, S. C. I. 9, 1149).

According to Markownikoff (B. 23, 3191), the stearoptene which separates from rose-oil melts at 36·5°, and has all the properties of a paraffin. It is perfectly odourless, and has no influence on the commercial value of the oil. The elæoptene consists of a mixture of two bodies, $C_{10}H_{20}O$ and $C_{10}H_{18}O$, of which only one, forming the bulk of rose-oil, possesses an alcoholic nature (S. C. I. 10, 63).

OUABAÏO. The poison of the Somalis. Along the whole of the west coast of Africa, especially in the country of the Somalis, occurs a tree used by the natives for the preparation of their arrow-poison, and called by them Ouabaïo. Its wood is yellowish-white, very hard and dense, odourless, but possessing a strong bitter taste. Arnaud has isolated from it (S. C. I. 1889, 211; 1888, 586) *ouabaïn*, $C_{30}H_{46}O_{12}$, which has a physiological action similar to that of strophanthin, $C_{31}H_{48}O_{12}$, but which is twice as toxic, the poisonous dose being about 0·2 mgrm. per kilo. of body-weight (S. C. I. 1888, 765)—Cathelineau, J. Pharm. Chem. 1889, 436; S. C. I. 9, 101.

OUTREMER. *Ultramarine* (*q. v.*); also PIGMENTS.

OXALIC ACID $C_2H_2O_4$, or $\left\{\begin{matrix}COHO\\COHO\end{matrix}\right.$.

This acid occurs as the acid potassium salt in wood-sorrel, garden rhubarb, and many other plants. As calcium oxalate, it occurs in many lichens and in certain urinary calculi, and in the free state is found in *Boletus igniarius* and in the juice of the chick pea.

It is obtained as an alkaline salt when an alkaline formate is gently heated, and as the ammonium salt when an aqueous solution of cyanogen is kept for some time. The sodium salt is produced by passing carbon dioxide over sodium heated to 360°. The free acid is one of the principal products of the action of nitric acid and other oxidising agents on organic matter.

Preparation.—In the laboratory, oxalic acid may be obtained by gradually adding 8 parts of nitric acid of sp.gr. 1·38 to 1 part of white sugar or starch, heating the mixture to boiling, and evaporating to about one-sixth the original bulk. The crystals obtained on cooling are recrystallised. If stronger acid be used the action is liable to become unmanageable.

This process was formerly employed on the manufacturing scale, but has now become superseded by a process consisting in the fusion of sawdust with potash. Starch, straw, bran, and other vegetable matters may be similarly treated, but the best results are obtained with sawdust, fir, pine, poplar, and other soft woods, giving better results than hard woods, such as oak and beech. In order to obtain a finer product the sawdust is sometimes (as in one of Dale's patents) treated with an alkaline lye to remove resinous and like bodies before fusion.

The largest yield is produced when the alkali employed is potash, but nearly equal results are obtained by the use of a proper admixture of potash and soda. The proportions employed by different firms vary considerably, and are usually kept secret. It is stated by Flack that potash and soda are employed in the proportion of 3 to 2 by Messrs. Roberts, Dale & Co., the pioneers of the sawdust process, while others state that they and Kuhnheim employ equal proportions. Sometimes as much as 2 parts of soda to 1 of potash is used. It is found that soda cannot be employed alone.

In the process employed by Roberts, Dale & Co., one part of sawdust is mixed with a caustic alkaline lye of sp.gr. 1·35, containing two or three parts of the mixed alkalis or of potash, and having been well mixed, is spread in thin layers on iron plates, heated by a flue beneath and exposed above to the air. After the mass has become dry, it swells up and evolves inflammable gas consisting of hydrogen, hydrocarbons, and vapours of a peculiar aromatic smell. After two or three hours the mass has acquired a dark-brown colour, and has become entirely soluble, but only contains from 1 to 4 p.c. of oxalic acid. Finally, however, after about six hours, a white or greyish mass is obtained which contains about 20 p.c. of the anhydrous acid. The temperature is not allowed to exceed 250°, or a considerable amount of oxalic acid may be lost. On this account it is impossible to decompose all the humus-like bodies produced at the commencement of the reaction, so that the mother-liquors require frequent regeneration.

In another process, a quantity of lime is slaked on the lye before mixture with the sawdust, and the heating is conducted on the bed of a reverberatory furnace with frequent raking to render the action uniform. The porous product consists mainly of calcium oxalate and alkaline carbonates, which may be lixiviated out, recausticised and used again. The calcium oxalate is decomposed by dilute sulphuric acid as described below.

The alkaline oxalates obtained by the first process may be treated with a small quantity of water to remove all the soluble substances except the sodium oxalate, or the whole may be dissolved in a minimum quantity of water, concentrated to 38°B., and allowed to crystallise. If too little alkali has been employed, the mother-liquor is so thickened by humus-like bodies as to interfere with the formation of the crystals and with their separation therefrom.

In a properly conducted operation, the mother-liquor is almost free from oxalates. It is recausticised, mixed with alkali to make up it strength, and used again, but the amount of organic matter then contained precludes its further use. It may then be concentrated to 40°B., mixed with enough sawdust to absorb it, and roasted on plates in a reverberatory furnace sufficiently to destroy all the organic matter except a certain proportion of carbon. The alkaline carbonates are then removed by lixiviation, recausticised, and again used.

The crystals obtained are dissolved and boiled for one or two hours with a slight excess of lime, until a portion of the solution, after filtration and acidulation with acetic acid, gives no precipitate with calcium chloride. The soda-lye thus obtained is used again. The calcium oxalate is washed once with water and filtered, and is then placed in large lead-lined vats, and mixed, with constant agitation, with sulphuric acid in the proportion of three equivalents to one equivalent of the oxalate. The pasty mass obtained is reduced to a thin paste with water, and well stirred and boiled until the liquid gives no indication of oxalic acid when tested.

The liquid is decanted, the last portions being filtered, and is concentrated to 15°B., removed from the calcium sulphate which then separates, and concentrated to 30°B. The mother-liquor obtained from the crystals separating on cooling is used for treating more lime.

The crude acid is usually somewhat dirty from adherent mother-liquor. It is separated therefrom by a centrifugal cleanser, washed with a minimum quantity of cold water, and recrystallised.

According to Thorn (D. P. J. 210, 24, and Ber. Ent. Chem. Ind. ii. 410), who has investigated the conditions under which oxalic acid is produced from sawdust, the greater yield is obtained with potash when thick layers of the mixture are heated, while a mixture of potash and soda, within certain limits, gives equally good results when thin layers are used.

The acid cannot be purified from oxalates by ordinary recrystallisation, but requires to be crystallised from hydrochloric acid of 10 to 15 p.c., which retains the bases as chlorides. A second crystallisation removes the acid. The pure acid may also be prepared by sublimation as described below, or by decomposing the methyl or ethyl ether with water.

Properties.—Oxalic acid crystallises in large transparent monoclinic prisms of sp.gr. 1·641 at 4° (Joule and Playfair), containing two molecules of water.

In an atmosphere dried by sulphuric acid, it gradually loses its water. The water is also gradually evolved and the crystals become opaque when heated at 60° or 70°. As the crystals melt in their water of crystallisation at 98°, and are then somewhat difficult to desiccate, it is advisable to dry the crystals at the lower temperatures. Saturated solutions of oxalic acid lose acid even on the water-bath. The anhydrous acid (dried as above) may be volatilised at 157°, and be thus obtained in pure white needles. The temperature should not be allowed to exceed 157°, as considerable decomposition ensues and an inferior product is obtained at 160°.

When oxalic acid is dissolved in 12 parts of warm concentrated sulphuric acid, the solution gradually deposits glistening rhombic pyramids of the anhydrous acid, which rapidly absorb two molecules of water and fall to powder.

Oxalic acid dissolves readily in water and in $2\frac{1}{3}$ parts of cold alcohol. It is also slightly soluble in ether but is insoluble in chloroform, benzene, and petroleum spirit. According to Alluard, the solubility in 100 parts of water is as follows:

8	parts	at	10°	75	parts	at	60°
13·9	,,	,,	20°	117·7	,,	,,	70°
23	,,	,,	30°	204·7	,,	,,	80°
35	,,	,,	40°	345	,,	,,	90°
51·2	,,	,,	50°				

Oxalic acid is a powerful reducing agent. The aqueous solution oxidises at the ordinary temperatures in presence of peroxide of lead and manganese. It precipitates gold from solution of the chloride, and, in sunlight, similarly reduces platinum chloride. In presence of sulphuric acid it is oxidised by potassium permanganate with production of carbon dioxide and manganese and potassium sulphates. Oxalic acid is not acted on by sulphuric acid at the ordinary temperature, but when heated with the strong acid it is decomposed into carbon monoxide and dioxide without darkening the acid. Phosphoric acid and phosphorus penta- and trichloride also cause the evolution of these gases. Chlorine is without action on the anhydrous acid, but in presence of water it is reduced to hydrochloric acid with evolution of carbonic acid. Hypochlorites and chlorides of easily reducible metals, such as gold and platinum, have a similar action, which explains the reducing action of oxalic acid on solutions of those metals.

Oxalic acid is completely converted into carbon dioxide and water when heated with nitric acid of sp. gr. 1·4 and upwards. It is reduced by nascent hydrogen to glyoxylic or glycollic acid.

Solutions of oxalic acid decompose carbonates, phosphates, chromates, &c., and even fluorspar. When heated with sodium or calcium chloride, the powdered acid liberates hydrochloric acid. Potassium and sodium, when heated with the dry acid, cause an evolution of hydrogen with production of a carbonate, the temperature rising to incandescence.

When heated with glycerine to from 70° to 90°, oxalic acid is converted into formic acid with evolution of carbon dioxide.

The commercial acid, and alkaline oxalates frequently contain organic matters which cause charring when heated alone or with sulphuric acid. Sulphates are usually present, and lead and other heavy metals frequently occur. Allen has found as much as 6·3 per cent. of lead oxide in a sample of the acid.

Oxalic acid is largely used as a 'discharge' in calico-printing and dyeing, and for bleaching flax and straw. It is also employed for whitening leather, for making formic acid and its ethers, and for removing ink or iron stains from fabrics, marble, &c. A solution of Prussian blue in oxalic acid is employed as a blue ink. Oxalic acid forms a constituent of several dyes. It has great cleansing power for brass and other metal, and even for woodwork, and forms a constituent of at least one of the recently-introduced soap-compositions for cleaning metals &c.

Detection and Estimation.—Solutions of lime salts, even of the sulphate, give precipitates of calcium oxalate, readily soluble in mineral acids but not in acetic acid, on addition to solutions of oxalates. Free oxalic acid is precipitated by lime water and calcium acetate, but it is better to render the solution alkaline by ammonia and acidulate with acetic acid before testing. Pure oxalic acid and oxalates do not char when heated alone or with concentrated sulphuric acid.

For estimating this acid, the hot dilute solution, free from mineral acids, or neutralised with ammonia and then acidulated with acetic acid, is precipitated with calcium chloride or acetate, or, when sulphates are present, with calcium sulphate. For the estimation in presence of interfering substances, reference must be made to standard works on analysis. After standing for twelve hours the precipitate is filtered off and dried, and is ignited at a dull, scarcely visible red heat to convert it into carbonate. A little saturated solution of ammonium carbonate is then added to reconvert into carbonate any of the substance which may have become causticised, and the mass is dried and ignited sufficiently to remove the whole of the ammonium salt. When the precipitate does not exceed a gram, it may be ignited at a bright-red heat over the blow-pipe and be weighed as oxide.

Another excellent method consists in dissolving the moist precipitate in dilute sulphuric acid and titrating with decinormal permanganate.

This permanganate method is applicable directly to the original substance, provided other oxidisable bodies are absent.

OXALATES.

This extensive series of salts includes both normal, acid, and double oxalates, and a class of acid salts known as quadroxalates, and apparently produced by the combination of one molecule of oxalic acid with one molecule of an acid oxalate. All oxalates decompose on heating, the alkaline salts forming carbonates. Only a limited number of oxalates are of technical importance.

Potassium oxalate $C_2O_4K_2.2H_2O$ crystallises in monoclinic prisms or pyramids, readily soluble in water. The *acid salt* C_2O_4HK is found in rhubarb, sorrel, and other plants. It occurs either in anhydrous, monoclinic prisms, or in triclinic crystals containing one molecule of water. The acid salt, which is much less soluble than the normal salt, forms with oxalic acid *potassium quadroxalate* $C_2O_4KH.C_2O_4H_22H_2O$, which forms triclinic crystals soluble in 20 parts of water at 20°.

Both these acid salts are sold as 'salts of sorrel' or 'salts of lemon,' and are used for removing ink stains, &c., and also for scouring metals, cleansing wood, &c., for which they are at least as suitable as the free acid.

The normal salt may be prepared by neutralising the acid with potash or potassium carbonate. The acid salt may be made by halving a solution of the acid, neutralising one part, and adding the other. The quadroxalate is similarly prepared by neutralising one-fourth of the solution and adding the remainder, or by adding 75 parts of potassium chloride to 252 parts of oxalic acid, both in saturated solution. Potassium oxalate is employed in the hot bath used in the Platinotype process, and is also used in other photographic operations (*v.* PHOTOGRAPHY).

Sodium oxalate $C_2O_4Na_2$ occurs in various plants growing in salt marshes. It and the acid salt are prepared similarly to the potassium compounds. No quadroxalate has yet been prepared. The normal salt requires about 36 parts of cold water for solution. It separates from hot solutions in fine glistening needles or as a crystalline powder. The acid salt is still less soluble.

Ammonium oxalate $C_2O_4(NH_4)_22H_2O$ occurs in Peruvian guano. It crystallises in long rhombic prisms readily soluble in water. The acid salt is less soluble, crystallises in rhombic prisms and gives a quadroxalate isomorphous with that of potassium. These salts are prepared similarly to the potassium salts.

Calcium oxalate C_2O_4Ca is widely distributed in the vegetable kingdom and is the least soluble of the calcium salts. It occurs in rhubarb and other plants, frequently in aggregations of needle-like crystals. In larger proportions it occurs in many lichens which grow on limestone, and in certain urinary calculi. It is precipitated as a powder containing one molecule of water, by addition of a calcium salt to an oxalate. When heated to 180° it becomes anhydrous, but it re-absorbs water when exposed to the air. The acid salt has not been prepared.

Barium and *strontium oxalates* resemble the calcium salts, but are somewhat soluble in water. The neutral *magnesium oxalate*, and double oxalates of magnesium with potassium and ammonium but not with sodium, are known. The acid magnesium oxalate has not been prepared.

Ferrous oxalate $C_2O_4FeH_2O$ occurs in lignite as *oxalite* or *humboldtine*. It may be prepared as a heavy yellow, nearly tasteless powder, almost insoluble in cold, and sparingly soluble in hot water, by mixture of ferrous sulphate with oxalic acid or an oxalate; or in fine lemon-coloured crystals by exposure of a solution of hydrous ferric oxide in oxalic acid. It is also slowly deposited from a solution of iron in oxalic acid. An acid oxalate appears to exist.

Ferrous oxalate is employed in *neutral* solution, as a developer in photography, and is sometimes used in medicine. When heated it is converted into a very finely-divided oxide, admirable as a rouge for optical purposes.

Ferric oxalate. The normal salt is slowly deposited as a yellow precipitate on mixture of a normal oxalate with ferric chloride or on treating freshly precipitated ferric hydroxide with a quantity of oxalic acid insufficient to dissolve the whole. The solution in oxalic acid gradually deposits ferrous oxalate on exposure to the light. Double salts with the alkalis are obtained by solution of ferric hydroxide in acid alkaline oxalates. The ferric ammonium oxalate is sometimes used instead of the double citrate for producing blue prints in photography.

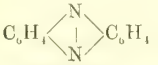
Antimony oxalates. The application of antimony oxalate and the double oxalates with the alkaline metals in calico-printing has been noted under article ANTIMONY, vol. i. The normal salt $Sb_2O_3.C_4O_62H_2O$ is obtainable by boiling antimonious chloride or oxychloride in oxalic acid, or by mixing a saturated solution of oxalic acid with a hydrochloric acid solution of the trichloride. It crystallises out as a granular precipitate. The antimony potassium oxalate $(C_2O_3)_3SbK_36H_2O$ is obtained in monoclinic crystals from a solution of antimonic acid in acid potassium oxalate. The sodium salt $(C_2O_4)_3SbNa_3C_2O_4Na_210H_2O$ is similarly prepared.

Cerium oxalate $Ce_2(C_2O_4)_39H_2O$ is a white, slightly granular, insoluble powder, permanent in the air, odourless and tasteless. It may be prepared by the action of oxalic acid solution on cerous oxide, or by addition of oxalic acid to a soluble cerium salt. Cerium oxalate has medicinal properties resembling those of bismuth subnitrate, and is used to prevent the vomiting of pregnancy and in certain diseases.

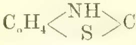
Methyl oxalate $C_2O_4(CH_3)_2$ is obtained in rhombic tables melting at 54° and boiling at 163° by dissolving anhydrous oxalic acid in methyl alcohol and washing the crystals with cold water. Methyl oxalate is converted into oxalic acid and methyl alcohol by boiling with water. Pure oxalic acid may thus be prepared. (Compare p. 577, vol. ii.)

Ethyl oxalate $C_2O_4\ (C_2H_5)_2$ is a liquid which may be obtained by slowly heating a mixture of 3 parts of the anhydrous acid and 2 parts of absolute alcohol to 100°, afterwards heating to 125° or 130° while the vapour of 2 parts of absolute alcohol is passed in. The ethyl oxalate is separated by fractional distillation. This compound is an aromatic oily liquid boiling at 186° and decomposed by water in the same manner as methyl oxalate.

OXAZINE COLOURING MATTERS. The azines or colouring matters of the saffranine group (*v.* AZINES, vol. i.) are derivatives of phenazine, while methylene blue and its allies are derived from thiodiphenylamine or thiazine (vol. ii.). The colouring matters of the present group are similarly derived from phenoxazine. The relationship of the parent compounds is shown by the following formulæ :—

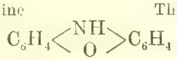


Phenazine



$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{S}{>}C_6H_4$

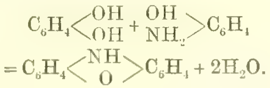
Thiazine



$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{O}{>}C_6H_4$

Phenoxazine.

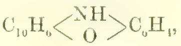
Phenoxazine itself was synthesised by Bernthsen (B. 1887, p. 942) by heating pyrocatechol and orthoamidophenol in a tube for forty hours to 260°-280°C. :—



$$C_6H_4{<}\genfrac{}{}{0pt}{}{OH}{OH} + \genfrac{}{}{0pt}{}{OH}{NH_2}{>}C_6H_4$$
$$= C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{O}{>}C_6H_4 + 2H_2O.$$

The parent-compound, like its analogues, phenazine and thiazine, is devoid of colouring properties.

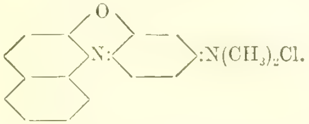
The first colouring matter of the group, a derivative of naphthophenoxazine,



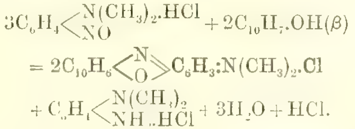
$$C_{10}H_6{<}\genfrac{}{}{0pt}{}{NH}{O}{>}C_6H_4,$$

was prepared by the action of nitrosodimethylaniline on *β*-naphthol (Meldola, B. 1879, p. 2065; C. J. Trans. 1881, p. 37), and is met with in commerce as **Meldola's Blue**; **New Blue** (Casella); **Cotton Fast Blue 2 B** (Actiengesell.); **Crystal Naphthylene Blue R** (Bayer & Co.); **Cotton Blue R** (Badische Co.).

This colouring matter, named '*β*-naphthol violet' by its discoverer, was originally prepared by heating nitrosodimethylaniline hydrochloride with *β*-naphthol in acetic acid solution and crystallising the hydrochloride from alcohol and hydrochloric acid. On the large scale the substances are simply boiled together in alcoholic solution, and the colouring matter precipitated by the addition of zinc chloride, with which it forms a double salt. The constitution of the colouring matter has been made the subject of an investigation by Nietzki and Otto (B. 1888, 1736), who assign the formula :—

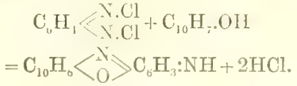


According to this view, the compound is formed by the action of three molecules of nitrosodimethylaniline[1] on two molecules of *β*-naphthol :—



$$3C_6H_4{<}\genfrac{}{}{0pt}{}{N(CH_3)_2.HCl}{NO} + 2C_{10}H_7.OH(\beta)$$
$$= 2C_{10}H_6{<}\genfrac{}{}{0pt}{}{N}{O}{>}C_6H_3{:}N(CH_3)_2.Cl$$
$$+ C_6H_4{<}\genfrac{}{}{0pt}{}{N(CH_3)_2}{NH_2.HCl} + 3H_2O + HCl.$$

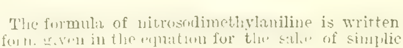
Some of the hydrogen is thus used up in reducing a portion of the nitroso- compound to dimethylparaphenylene-diamine, the latter having been discovered by Nietzki and Otto as a by-product of the reaction. These investigators have, moreover, prepared the unmethylated parent-compound of the present colouring matter by the action of quinonedichlorimide on *β*-naphthol :—



$$C_6H_4{<}\genfrac{}{}{0pt}{}{N.Cl}{N.Cl} + C_{10}H_7.OH$$
$$= C_{10}H_6{<}\genfrac{}{}{0pt}{}{N}{O}{>}C_6H_3{:}NH + 2HCl.$$

The commercial product is a dull bronzy-violet powder consisting of the zinco-chloride. It is readily soluble in water with a deep violet colour, the solution becoming blue on adding hydrochloric or sulphuric acid. Alkalis precipitate the free base in the form of a brown resinous substance. The colouring matter dissolves in strong sulphuric acid with a dirty-green colour, becoming blue on dilution. It imparts an indigo-blue colour to cotton mordanted with tannin and tartar emetic.

Cyanamines. It has recently been shown by Witt (B. 1890, 2247) that the free base of this and analogous colouring matters readily becomes transformed on heating into other coloured compounds to which he has assigned the above name. The cyanamine from *β*-naphthol violet forms crystalline salts, having a metallic lustre and dissolving with a bluish-green colour instead of the violet colour characteristic of the original compound. The free base is insoluble in most solvents, whereas the oxazine base is soluble in ether, &c. The formation of the cyanamine is probably due to condensation between two molecules of nitrosodimethylaniline and one molecule of *β*-naphthol, with the elimination of two molecules of water. Witt assigns to the free base the formula $C_{26}H_{25}N_4O_2$, and to the hydrochloride the formula $C_{26}H_{26}N_4OCl_2$, suggesting as constitutional formulæ :



$$(CH_3)_2N.C_6H_4.N.C_{10}H_5.N.C_6H_4.N(CH_3)_2.OH$$

and

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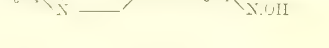
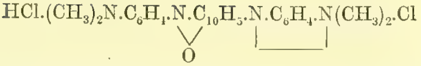
[1] The formula of nitrosodimethylaniline is written in the form given in the equation for the sake of simplicity only. The free base and the hydrochloride may have the respective constitutions :

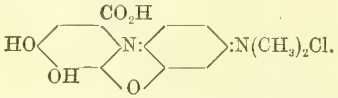




$$HCl.(CH_3)_2N.C_6H_4.N.C_{10}H_5.N.C_6H_4.N(CH_3)_2.Cl$$

Colouring matters identical with or related to the cyanamines have also been obtained by R. Hirsch by the action of ammonia or other amines on the oxazines (B. 1890, 2992).

Gallocyanin; Solid Violet (Durand and Huguenin). Introduced in 1881 by H. Köchlin, and prepared by the action of nitrosodimethylaniline hydrochloride on gallic acid. The original patent claims the products formed by the action of the nitroso- compound on gallic acid, tannin, or tannic acid, catechuic acid, and analogous compounds, but the first appears to be the compound of the greatest technical importance. It is prepared by boiling the constituents in aqueous solution till the reaction is complete, and then throwing out the colouring matter with common salt. Its constitution, according to Nietzki, is expressed by the formula:—



The formation is expressed by the equation:—

$$3C_6H_4{<}{}^{N(CH_3)_2}_{NO} + 2C_6H_2{\lessgtr}{}^{COOH}_{(OH)_3}$$
$$= 2C_{15}H_{12}N_2O_5 + C_6H_4{<}{}^{N(CH_3)_2}_{NH_2} + 3H_2O.$$

The commercial product is a greenish paste insoluble in water, but soluble in alcohol, with a bluish violet colour. The paste dissolves in hydrochloric acid with a magenta-red, and in strong sulphuric acid with a bright blue colour becoming red on dilution. The substance dissolves in caustic soda with a reddish-violet colour.

Literature.—H. Köchlin, Germ. pat. 19,580, Dec. 17, 1881, Ber. 1882, p. 2645; Chem. Ind. 1882, p. 327; Mon. Sci. 1883, p. 292; Bull. Soc. Ind. Mul. 1883, p. 206. Reverdin and Noelting, 'Sur la Constitution de la Naphthaline, &c.,' 1888, p. 71. Nietzki and Otto, B. 1888, p. 1736.

Prune. This colouring matter, discovered by Kern in 1886, is the methyl ether of the preceding compound, and is prepared by the action of nitrosodimethylaniline on methyl gallate. Its formula is therefore

$$C_6H(OH)_2(COOCH_3){<}{}^{N}_{O}{>}C_6H_3{:}N(CH_3)_2.Cl.$$

The mode of formation is similar to that of gallocyanin. The methyl ether of gallic acid is prepared by passing dry hydrochloric acid gas into the solution of the acid in methyl alcohol. The colouring matter is prepared by heating the methyl ether with nitrosodimethylaniline hydrochloride in ethyl or methyl alcohol or in water as a solvent. The compound forms brown glittering crystals or a dark-brown powder, readily soluble in water with a violet colour, becoming magenta red on the addition of hydrochloric acid. The addition of caustic soda to the aqueous solution causes at first a brown precipitate, which dissolves into a violet solution on adding more of the reagent. The substance dissolves in strong sulphuric acid with a bright blue colour becoming red on dilution.

Literature.—Kern, Eng. pat. 5,953, April 23, 1887; S. C. I. 1888, p. 385. Germ. pat. (Kern and Sandoz) 45,786, April 3, 1887.

Muscarin (Durand and Huguenin). Discovered by Annaheim in 1885, the colouring matter being prepared in the usual way by the action of nitrosodimethylaniline on the dioxynaphthalene (m.p. 186°) of Ebert and Merz. The compound is thus the hydroxy- derivative of β-naphthol violet (Meldola's Blue) and its formula is:—$HO.C_{10}H_5{<}{}^{N}_{O}{>}C_6H_3{:}N(CH_3)_2Cl.$

The commercial product forms a brownish-violet powder sparingly soluble in cold, but readily in hot, water, with a violet colour, the solution giving a violet precipitate with hydrochloric acid, and a yellowish-brown solution with caustic soda. The colouring matter dissolves in strong sulphuric acid with a bluish-green colour, becoming blue on dilution, then, on continuing the addition of water, passing into violet, and finally giving a violet precipitate.

Nile Blue (Badische Co.). This colouring matter is prepared by the action of nitrosodimethyl-*m*-amidophenol hydrochloride on α-naphthylamine. It was discovered by Reissig in 1888. The nitroso- compound from which the dye stuff is prepared is made by treating dimethyl- (or diethyl-) *m*-amidophenol with the necessary quantity of sodium nitrite and hydrochloric acid in a well-cooled aqueous solution. The colouring matter is prepared in the usual way by heating the constituent materials in a solvent such as acetic acid, dilute hydrochloric acid, &c. The shade becomes greener if alkylated naphthylamines are used instead of naphthylamine. From the mode of formation of this colouring matter it follows that it may be regarded as a basic analogue of muscarine containing NH_2 instead of the hydroxyl group:—

$$(\alpha)NH_2.C_{10}H_5{<}{}^{N}_{O}{>}C_6H_3{:}N(CH_3)_2Cl.$$

The commercial product is the sulphate of the foregoing base, and forms a greenish bronzy crystalline powder, slightly soluble in cold, and readily soluble in hot water with a blue colour. The addition of hydrochloric acid to the aqueous solution causes the separation of needle-shaped crystals which appear violet by transmitted and green by reflected light. The free base is thrown down in the form of a red precipitate on adding dilute caustic soda to the aqueous solution. The colouring matter dissolves in strong sulphuric acid with a yellow colour passing into green and then into blue on dilution.

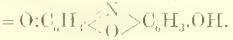
Literature.—Badische Anilin- u. Soda-Fabrik, Eng. pat. 4,476, March 23, 1888 (S. C. I. 1889, p. 280); Germ. pat. 45,268, February 28, 1888.

Fluorescent blue; resorcin blue (Bindschedler and Busch). This colouring matter belongs to a group of substances obtained by the action of nitrous acid on phenols, and has only recently been proved by the researches of Nietzki, Dietze, and Mäckler to belong to the oxazines. In 1871, Weselsky obtained a compound by the action of nitrous acid on resorcinol which he named 'diazoresorcin,' and to which he assigned the formula $C_{18}H_{12}N_2O_6$. By the action of concentrated acids this compound loses water and becomes transformed into a substance to which Weselsky gave the name 'diazoresorufin' and the formula $C_{36}H_{18}N_4O_9$. In 1874, Liebermann discovered that strong sulphuric acid in which a small quantity of a nitrite had been dissolved, when heated with phenolic substances, gave rise to colouring matters which are at the present time known as Liebermann's phenol colouring matters. None of these are of any technical importance excepting the compounds of Weselsky above referred to, which belong to the same group. In 1874, Weselsky and Benedikt continued the investigations with other phenols, and, in 1880, the firm of Bindschedler and Busch patented the manufacture of a colouring matter by acting with sodium nitrite upon resorcinol dissolved in sulphuric acid and then brominating the product. This colouring matter is the fluorescent or resorcin blue of the market. The composition of the 'diazoresorcin' was again investigated in 1881 by Weselsky and Benedikt, and the formula $C_{18}H_{10}N_2O_6$ assigned to it. The most recent researches of Nietzki, Dietze, and Mäckler have shown that neither 'diazoresorcin' nor 'diazoresorufin' are diazo- compounds, and they have therefore substituted for these names those of 'resorufin' and 'resazurin' respectively. They assign the formula:

Resorufin—$C_{12}H_7NO_3$. Resazurin—$C_{12}H_7NO_4$.

The constitutional formula of resorufin represents it as an oxyoxazine derivative resulting from the action of nitrosoresorcinol (regarded as hydroxyquinoneoxime) on resorcinol:

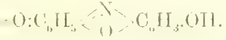
$$O:C_6H_3(OH):N.OH + C_6H_4(HO)_2 - 2H_2O$$



$$= O:C_6H_3 < \genfrac{}{}{0pt}{}{N}{O} > C_6H_3.OH.$$

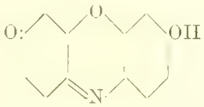
It is probable that the reaction takes place in two stages, an indophenol being first formed:

$$\text{I.}\quad O:C_6H_3(OH):N.OH + C_6H_4(HO)_2 - H_2O$$
$$= O:C_6H_3(OH):N.C_6H_3(HO)_2.$$
$$\text{II.}\quad O:C_6H_3(OH):N.C_6H_3(HO)_2 - H_2O$$

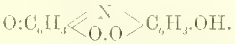


$$= O:C_6H_3 < \genfrac{}{}{0pt}{}{N}{O} > C_6H_3.OH.$$

The constitution is more fully expressed by the formula:

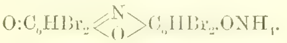


The constitution of resazurin has not yet been made out with certainty, but it is suggested that it contains two atoms of oxygen linked together as in the formula:



$$O:C_6H_3 < \genfrac{}{}{0pt}{}{N}{O.O} > C_6H_3.OH.$$

Resorufin itself is not adapted for dyeing purposes, as its colouring properties only appear in neutral or alkaline solutions, which are of a red colour with a strong red fluorescence. The commercial product is prepared by dissolving the resorufin in potassium carbonate, adding the necessary quantity of bromine and then acidifying. The resorufin takes up four atoms of bromine, forming a strongly acid colouring matter which is sent into commerce as the ammonium salt. The formula is:



$$O:C_6HBr_2 < \genfrac{}{}{0pt}{}{N}{O} > C_6HBr_2.ONH_4.$$

The resorufin is prepared by heating 10 parts of resorcinol with 50 parts of strong sulphuric acid saturated with nitrous acid to 100°C., and then diluting with water. Or nitrosoresorcinol is first prepared by acting on sodium-resorcinol with amyl nitrite and the nitroso- derivative heated with resorcinol and sulphuric acid to 100°. The product is brominated in the manner described.

The colouring matter is met with as a 10 p.c. paste containing metallic-green needle-shaped crystals. It dissolves in boiling water with a blue colour, showing a strong red fluorescence. Mineral acids added to the aqueous solution precipitate the free acid as a reddish-brown powder. It dissolves in strong sulphuric acid with a blue colour, which, on dilution of the acid, becomes first violet, and then a reddish-brown separates.

Literature.—Weselsky (B. 1871, 32, 613; A. 162, 273; Liebermann (B. 1874, 247, 1098); Baeyer and Caro (B. 1874, 966); Weselsky and Benedikt (B. 1874, 439, 445; B. 1881, 530; and B. 1885, iii. 76); Brunner and Krämer (B. 1884, 1847, 1867, and 1875; B. 1885, 580); Nietzki, Dietze, and Mäckler (B. 1889, 3020).

Patent.—Bindschedler and Busch, Germ. pat. 14,622, December 30, 1880 (B. 1881, 1589).

Lackmoïd. A blue colouring matter, probably belonging to the oxazine group obtained by heating resorcinol with sodium nitrite. The constitution is unknown, and the empirical formula is assigned as $C_{12}H_9NO_4$ (?). The commercial product is a dark-violet granular powder soluble in water with a bluish violet colour, and in alcohol with a blue colour and dark-green fluorescence. Mineral acids cause a dirty-red precipitate when added to the aqueous solution. Sometimes used as an indicator in alkalimetry.

Literature.—Benedikt and Julius (M. v. 534; B. 1884, iii. 492); Traub and Hock (B. 1884, 2615); Wurster (B. 1887, 2631, 2934).

The following patents relating to the colouring matters of this and allied groups may be consulted:—Germ. pat. 40,372, Sept. 7, 1886, H. M. Baker, B. 1887, iii. 616; Germ. pat. 40,886, Sept. 23, 1886, Durand and Huguenin, B. 1887, iii. 756; Germ. pat. 40,897, Jan. 5, 1887, H. J. Walder, B. 1887, iii. 756; Germ. pat. 41,512, Feb. 4, 1887, Farb. vorm. F. Bayer & Co., B. 1888, iii. 72; Germ. pat. 47,549, March 18, 1888, Durand and Huguenin, B. 1889, iii. 463; Germ. pat. 50,612, Jan. 5, 1889, Leonhardt & Co., B. 1890, iii. 220; and Eng. pat. 8,264, May 17, 1889, S. C. I. 1890, 497; Germ. pat. 48,996, Feb. 19, 1889, Geigy & Co., B. 1889, iii. 851; and Eng. pat. 2,941, Feb. 19, 1889, S. C. I. 1889, 981; Germ. pat. 50,998, July 23, 1889, Gesell. f. Chem. Ind. in Basel, B. 1890, iii. 309; Eng. pat. 11,848, July 25, 1889, S. C. I. 1890, p. 610; Germ. pat. 54,114, Sept. 22, 1889, Durand and Huguenin, B. 1891, iii. 250; Eng. pat. 15,360, Sept. 30, 1889, S. C. I. 1889, p. 981; Eng. pat. 583, Jan. 12, 1891, S. C. I. 1891, p. 359; Germ. pat. 52,045, Nov. 9, 1889, Dahl & Co., B. 1890, iii. 534; Eng. pat. 569, Jan. 11, 1890, Kern and Sandoz, S. C. I. 1891, 131; Eng. pat. 4,577, March 24, 1890, Farb. vorm. Meister, Lucius, and Brüning, S. C. I. 1891, p. 249; also Eng. pat. 5,777, April 16, 1890, ibid. p. 249; Germ. pat. 54,658, March 25, 1890, Casella & Co., B. 1891, iii. 380; Eng. pat. 6,946, May 5, 1890, Casella & Co., S. C. I. 1891, p. 359; Eng. pat. 18,526, Nov. 17, 1890, Durand and Huguenin, S. C. I. 1891, p. 133. R. M.

OX-GALL *v.* Gall.

OXONITE *v.* Explosives.

OXYACANTHINE $C_{18}H_{19}NO_3$. An alkaloid associated with berberine and berbamine in berberis root (Hesse, B. 19, 3190).

OXYANTHRARUFIN. *Oxychrysazin v.* Alizarin and allied colouring matters.

OXYAZO- DYES *v.* Azo- dyes.

OXYCANNOBIN *v.* Resins.

OXYGEN. Sym. O. At. wt. 15·96.

Historical note.—Mayow in 1674 recognised that the *active* constituent of air which supports combustion forms only part of the atmosphere, and that the same substance is present in nitre, and is given off when nitre is heated strongly. Mayow termed this gaseous constituent of air and nitre *spiritus vitalis*, *spiritus nitro-aëreus*, and *pabulum igneo-aëreum.* But it was just a century later before its actual discovery took place. Priestley first obtained the gas on August 1, 1774, by heating mercuric oxide in a glass vessel by the heat of the sun's rays concentrated on the oxide by means of a burning glass, and gave it the name *dephlogisticated air.* The gas was isolated independently, and almost simultaneously, by the Swedish chemist Scheele, who applied to it the term *empyreal* or *fire-air.* Condorcet soon after suggested the name *vital air.* Lavoisier regarded it as an essential constituent of all acids, and hence gave it its present name *oxygen* (from *ὀξύς*, acid, and *γεννάω*, I form). The later discovery that hydrochloric and the other halogen acids contained no oxygen showed that this substance is not necessarily present in acids, but the name has been retained. The discovery of oxygen was the means of leading Lavoisier to the true theory of combustion.

Occurrence.—Oxygen is the most abundant, and the most widely distributed element in nature. In the free state it occurs, mechanically mixed with nitrogen, in the atmosphere, of which it forms about 21 p.c. by volume, and more than 23 p.c. by weight. In the combined state it forms eight-ninths by weight of all the water on the globe, and nearly half of the three chief constituents of the earth's crust, viz., silicious rocks, chalk, and alumina. Most minerals—the chief exceptions being rock salt, fluorspar, blende, galena, and pyrites—contain oxygen in considerable proportions. It is an essential constituent of all animal and vegetable tissues and fluids. It is absorbed in large quantities from the atmosphere by animals and vegetables during respiration, but this abstraction is practically counterbalanced by the oxygen evolved by green foliage under the influence of sunlight.

Preparation.—A. *On the laboratory scale.* Oxygen may be obtained by the action of heat on the oxides of mercury, silver, gold, and platinum; the peroxides of hydrogen, barium, lead, and manganese; the chlorates, bromates, iodates, nitrates, and bichromates of potassium and other bases; it is evolved during some chemical reactions, and during the electrolysis of many substances, notably of water.

Of the modes of preparation most convenient for use in the laboratory, or of interest from historical or theoretical considerations, the following are the principal:—

(1) By heating red oxide of mercury it splits up into vapour of mercury (which condenses) and oxygen: $2HgO = 2Hg + O_2$. This reaction is of interest as being that by which Priestley first obtained oxygen.

(2) By heating manganese dioxide to a bright-red heat it gives up one-third of its oxygen: $3MnO_2 = Mn_3O_4 + O_2$. The oxide is best heated in an iron bottle placed in a furnace, as glass vessels will not stand the high temperature required. 100 parts by weight of the pure peroxide yield 12·3 parts by weight of oxygen.

Manganese dioxide occurs in large quantities in nature as the mineral *pyrolusite*, and thus forms a cheap source for the preparation of quantities of a few hundred feet of oxygen, but the high temperature required makes the process somewhat inconvenient. Pyrolusite usually contains about 70 p.c. of the dioxide, and therefore gives a lower yield of oxygen than that indicated by the equation.

(3) Potassium chlorate is a very convenient and economical source for small quantities of oxygen for lecture and laboratory purposes. When gradually heated in a hard glass retort or flask, this salt melts at about 360–370°, and at about 370–380°C. evolution of oxygen commences. After some time the fused mass thickens from the formation of the perchlorate, which, at a still higher temperature, is also decomposed. Ultimately, therefore, potassium chloride alone remains in the generating flask, the whole of the oxygen having been given off according to the equation: $2KClO_3 = 2KCl + 3O_2$. 100 parts by weight of chlorate yield 39·18 parts by weight of oxygen, or 1 oz. of chlorate 1·7 gallons of the gas.

The temperature required in this decomposition is too high for convenient use, as the glass vessels employed in the preparation of the gas often soften under the great heat, and yield to the pressure of the contained gas. When metallic vessels are used the heating must be very carefully watched, since, the decomposition being exothermic (*i.e.* heat being evolved during the reaction), when once decomposition has set in, the evolution of gas is liable to become very violent. If the potassium chlorate be mixed with about one-eighth its weight of some non-fusible oxide such as oxide of copper, oxide of iron, or manganese dioxide, the evolution of oxygen takes place at about 240°, or considerably below that at which the salt fuses, and is much more regular. The addition of a little spongy platinum answers the same purpose.

The gas prepared in this way almost invariably contains traces of chlorine, which are removed, when necessary, by passing the gas through a solution of caustic soda.

Commercial manganese dioxide (pyrolusite), is sometimes adulterated with coal-dust. If such dioxide is heated with potassium chlorate the coal-dust burns—often with explosive violence—at the expense of the oxygen of the chlorate, and this has been the cause of fatal accidents. It is, therefore, advisable to test the dioxide before use by heating a small quantity in a test tube with some chlorate.

The action of these oxides in facilitating the decomposition of the potassium chlorate is not thoroughly understood. It is probably due to the transient formation of higher oxides of extreme instability. The oxides which show this action most markedly are those which form unstable higher oxides. The action of spongy platinum is still less clear, but is probably connected with the tendency of that substance to condense oxygen on its surface.

(4) By heating a concentrated solution of bleaching powder (or any hypochlorite) to which a small quantity of oxide of cobalt has been added, it is resolved into calcium chloride and oxygen: $2CaOCl_2 + 4CoO = 2CaCl_2 + 2Co_2O_3$ and $2Co_2O_3 = 4CoO + O_2$. The decomposition is shown in two stages to exhibit the action of the oxide of cobalt. It is not necessary to use pre-formed oxide of cobalt, as any salt of cobalt will answer the same purpose. The oxides of copper, iron, and nickel are similar in their action. Instead of a solution a thick paste of bleaching-powder and water may be used if a small quantity of paraffin oil is added. The oil, floating on the surface of the pasty liquid, prevents the frothing which would otherwise take place. The best temperature for the evolution of gas is about 70–80°, at which a steady stream may be obtained.

Another modification of this method is to pass a stream of chlorine into boiling milk of lime to which a small quantity of a salt of copper, cobalt, or nickel has been added. Oxygen gas is given off according to the equation $2Cl_2 + 2Ca(OH)_2 = 2CaCl_2 + 2H_2O + O_2$.

(5) When an intimate mixture of 3 mols. barium chloride (2 parts by weight) and 1 mol. potassium bichromate (1 part by weight) is treated with dilute sulphuric acid, oxygen is abundantly evolved at ordinary temperatures (Robbins, P. J. [2] 5, 436).

(6) If 2 pints of commercial hydrogen peroxide (3 p.c. solution) and 1 lb. of dilute sulphuric acid of sp.gr. 1·5 are introduced into a suitable generating flask, and a solution of 800 grains of potassium permanganate in 28 fluid ounces of water is allowed to flow gradually into the mixture from a dropping funnel, oxygen will be rapidly evolved without the application of heat, the amount of oxygen obtained from these quantities being about 5 gallons.

(7) On passing a mixture of steam and chlorine through a red-hot porcelain tube, filled with fragments of porcelain to increase the heating surface, the chlorine combines with the hydrogen of the water and oxygen is liberated: $2H_2O + 2Cl_2 = 4HCl + O_2$.

(8) A convenient method of obtaining small quantities of oxygen is by the action of water on a mixture of barium peroxide and potassium ferricyanide (G. Kassner, Zeits. f. angew. Chem. 1890, 448).

6·58 grams finely powdered potassium ferricyanide is intimately mixed with 2·25 grams of 75 p.c. barium peroxide. When this is moistened with water, oxygen is evolved at the ordinary temperature, a crystalline magma of potassium barium ferrocyanide being left: $K_6Fe_2Cy_{12} + BaO_2 = K_6Ba(FeCy_6)_2 + O_2$. 1·4 grams of ferricyanide yields a litre of oxygen.

(9) By the electrolysis of water slightly acidulated with sulphuric acid, the water is resolved into hydrogen and oxygen, the latter appearing at the positive pole: $2H_2O = 2H_2 + O_2$. This forms a convenient method of obtaining small quantities of pure oxygen, such as are required in gas analysis.

10. Oxygen may be prepared from such highly oxidised compounds as peroxides of lead and manganese, bichromate and permanganate of potash, &c., by the action of sulphuric acid on these substances. These are, however, seldom used as sources of gaseous oxygen, but are very useful as oxidising agents. Thus hydrochloric acid, when treated with sulphuric acid and potassium permanganate, is oxidised to hypochlorous acid, and alcohol treated with sulphuric acid and manganese dioxide yields aldehyde and water. The following equations represent the changes which take place when manganese dioxide and potassium bichromate are respectively treated with sulphuric acid:

$$2H_2SO_4 + 2MnO_2 = 2MnSO_4 + 2H_2O + O_2$$

and

$$8H_2SO_4 + 2K_2Cr_2O_7 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2.$$

The change is rendered visible in the latter case by the formation of a deep-green salt of chromium, the solution being previously of a red colour.

11. When fresh leaves, such as mint or parsley, are exposed to the influence of sunlight in an inverted cylinder filled with water saturated with carbon dioxide and standing in a basin of the same liquid, oxygen appears after a time in minute bubbles on the leaves, and collects in the upper part of the jar. This method of liberating oxygen is of interest as being that which occurs in nature, by means of which the loss of atmospheric oxygen continually taking place from combustion and respiration is replaced.

Several other modes of preparation which, in addition to their theoretical interest, are of practical and technical value, will be treated of in the following section.

B. *On the industrial scale.* 1. The first method proposed for obtaining oxygen on the large scale was the ignition of nitre, and this method, in various modifications, has formed the basis of several patents. The first oxygen patent occurring in the records of our Patent Office, is No. 12,536, S. White, 1849. But the oxygen so obtained is contaminated with oxides of nitrogen, and this method has not proved advantageous. It deserves mention, however, as being the means by which Priestley first obtained impure oxygen in 1771. He then believed the gas to be 'fixed air' (carbon dioxide), and only recognised his mistake three years afterwards, when he obtained oxygen from mercuric oxide.

2. By heating manganese dioxide. This was until recently one of the cheapest methods of preparing oxygen on the commercial scale.

3. By heating a mixture of potassium chlorate and about one-eighth of its weight of manganese dioxide. Though more costly than the last-named, this method is more easily carried out, and was, until within the last year or two, almost always employed in the preparation of the considerable quantities of oxygen used for lime-light purposes.

4. By the electrolysis of water. This method has formed the basis of many patents taken out

for the production of oxygen, and was for a time used practically on a commercial scale. But the large and inevitable loss attending the conversion of heat into power, and power into electrical force, and the need for skilled labour, makes the process too expensive, and there is but little likelihood of these drawbacks being overcome.

5. By the decomposition of sulphuric acid by heat: $2H_2SO_4 = 2SO_2 + 2H_2O + O_2$. The sulphuric acid is allowed to drop on red-hot surfaces, and is thus decomposed. If the oxygen alone is wanted, the emergent gaseous mixture is passed over media suitable for the absorption of the water and sulphur dioxide. As a method for the preparation of oxygen only this process has not found much favour, but it has been very largely and successfully used in the preparation of sulphuric anhydride, where, the water being removed by a desiccating agent, a mixture of sulphurous anhydride and oxygen in the desired proportions is at once obtained. It is the process suggested by Squire in his patent for the manufacture of sulphuric anhydride (Eng. pat. 3,278, 1875) as the best for that purpose.

6. By the dialysis of air. Many attempts have been made to utilise the laws of diffusion of gases through porous septa, discovered by Graham, or the property of caoutchouc when in thin layers to allow oxygen to pass through it more readily than nitrogen. Several patents have been taken out for processes of this kind, but with no practical success, and the phenomena do not seem likely to lend themselves to the production of oxygen on the large scale.

7. Better success has attended the endeavour to make use of the greater solubility of oxygen than of nitrogen in water or other solvents. Mallet, who took out a patent for this process (Eng. pat. 2,137, 1869), compressed the air over water. The coefficient of solubility of oxygen in water is ·046, of nitrogen ·025. The oxygen was, therefore, dissolved in greater proportion than the nitrogen, and when the excess of pressure was removed and the dissolved gases extracted by the aid of a vacuum pump, the amount of oxygen in the gaseous mixture was greater than in air. This mixture was then repeatedly subjected to the same treatment, when, after about eight absorptions, nearly pure oxygen was obtained. The following table, given by Mallet (D. P. J. 199, 112), shows the composition of the gaseous mixture at each successive stage of the operation:—

Atmospheric air	Composition after successive absorptions							
	1	2	3	4	5	6	7	8
N = 79 . . .	66·7	52·5	37·5	25	15	9·	5	2·7
O = 21 . . .	33·3	47·5	62·5	75	85	91·	95	97·3

This process was used by Phillips in 1871–72 to obtain oxygen for his experimental lighting of part of Cologne by special oxygen-fed oil lamps, but beyond this does not appear to have been practically applied.

8. By the alternate oxidation and de-oxidation of cuprous chloride. Cuprous chloride, if exposed to air, and especially to moist air, is oxidised to cupric oxychloride, and this, when heated to dull redness, gives off oxygen, and is reconverted into cuprous chloride. (*a.*) $2Cu_2Cl_2 + O_2 = 2Cu_2OCl_2$, (*b.*) $2Cu_2OCl_2 = 2Cu_2Cl_2 + O_2$.

Mallet obtained patents (Eng. pat. 2,934, 1865, and 3,171, 1866) for the practical utilisation of this method as a continuous process for obtaining oxygen from the air, but it has not been found economically available on the large scale.

9. By the alternate formation and decomposition of alkaline manganates. When an oxide of manganese is mixed in suitable proportions with a caustic alkali (potash or soda), and is subjected to the action of air at a moderately high temperature, an alkaline manganate is formed. If this manganate is then heated to a bright-red heat, and a current of steam passed over it, it is resolved into its original constituents with evolution of oxygen (C. M. Tessié du Motay and C. R. Marechal, Eng. pat. 85, 1866).

$$2MnO_2 + 4NaOH + O_2(air) = 2Na_2MnO_4 + 2H_2O\ ;$$
$$2Na_2MnO_4 + 2H_2O = Mn_2O_3 + 4NaOH + 3O\ ;$$
$$Mn_2O_3 + 4NaOH + 3O(air) = 2Na_2MnO_4 + 2H_2O.$$

The mixture was introduced into horizontal retorts, which were heated to a dull-red heat whilst a current of air was passed through. After oxidation was complete the supply of air was cut off, the retorts were heated to a bright-red heat, and a current of steam admitted when oxygen was evolved. The retorts were then allowed to cool again to a dull red, the passage of air again commenced, and so on. The mixture was said to undergo no deterioration, and a continuous and very economical method of obtaining oxygen seemed attained. Works were erected, and the process carried out on the large scale at Paris, Lille, Brussels, Vienna, and New York, and large quantities of oxygen were made. A large part of Paris was laid with a double system of piping with the intention of lighting that city with the oxy-hydrogen light, and the New York Company carried out by the same light the lighting of the works during the building of the Brooklyn bridge. But it was found in practice that the mixture did deteriorate, the yield of oxygen rapidly diminishing, and finally almost ceasing. This was probably due to the difficulty of maintaining the intimate mixture of the easily-fusible hygroscopic and very soluble soda with the manganic oxide, the former settling to the bottom through the combined effect of the heat and steam used.

Recently Bowman (Eng. pat. 7,851, 1890) claims to have overcome this difficulty by making the alkaline manganate in a granular form and dusting over the granules, whilst still in a plastic condition, with oxide of copper.

10. Kassner (Eng. pat. 11,899, 89) has found that when an intimate mixture of lead oxide and chalk is heated to 600° in contact with the air, a calcium plumbate $CaPbO_4$ is formed. If this plumbate is then introduced into a solution of

potassium or sodium carbonate it is decomposed, an insoluble precipitate of calcium carbonate and lead peroxide is formed, and caustic potash or soda remains in solution. This is removed by decantation, and the precipitate washed. The precipitate, in which the lead peroxide is, of course, the active part, may then either be used directly as an oxidant, or it may be introduced into a decomposing vessel, dried with superheated steam, and heated to about 500°, when oxygen is evolved, the mixture of lead oxide and calcium carbonate left being then ready for regeneration. The decomposition of the plumbate may also be effected by suspending it in water and treating with carbonic acid. The following equations indicate the reactions taking place:

$$2CaCO_3 + PbO + O(\text{air}) = Ca_2PbO_4 + 2CO_2\,;$$
$$Ca_2PbO_4 + 2Na_2CO_3 + 2H_2O$$
$$= 4NaOH + 2CaCO_3 + PbO_2\,;$$
$$2CaCO_3 + PbO_2 = 2CaCO_3 + PbO + O.$$

The inventor lays stress on the cheapness of the process owing to the caustic soda obtained being a valuable by-product. The complexity of the process and the large amount of labour entailed by it, leave very little chance of its being practically applicable, except possibly in chemical works, where it is used in conjunction with the manufacture of caustic alkali, and even here its economy is very doubtful.

The decomposition of the plumbate into lime and lead peroxide may also be effected *in situ* by means of a current of moist furnace gases at 80–100°, and the oxygen then liberated by raising the temperature. The great changes of temperature, however, thus involved, would certainly render the method impracticable, and in addition the sulphur impurities in the furnace gases would undoubtedly rapidly deteriorate the mixture.

Salamon (Eng. pat. 6,553, 1890) proposes to decompose the calcium plumbate without removing it from the producer in which it is formed by allowing the temperature to fall 'to a certain point,' and then introducing a current of pure carbon dioxide. The following reaction then occurs: $Ca_2PbO_4 + 2CO_2 = 2CaCO_3 + PbO + O$. This necessitates the use of at least four times the volume of carbon dioxide as of oxygen obtained, a condition which at once puts the process out of the question as a technical and economical one. It has been suggested that the quantity of pure carbon dioxide required may be largely reduced by carrying out the earlier part of the reaction by means of the carbon dioxide in furnace gases, and using it pure only at the last. But the drawbacks so introduced would fully neutralise any advantage.

11. By the alternate formation and decomposition of barium peroxide. In 1851 Boussingault found that when barium oxide (baryta) is heated to a dull-red heat in a current of air it is converted into barium peroxide, and that at a higher temperature this peroxide is again resolved into barium oxide and oxygen. But his attempts to utilise this reaction as a practical and economical source of oxygen failed owing to the fact that after a few oxidations and deoxidations the baryta lost its power of re-absorbing oxygen. Many other attempts were made to overcome this difficulty, but for long without success. In 1879, however, the MM. Brin frères were successful, and took out a patent for the process (Eng. pat. 1,416, 1880). Further improvements were made by the MM. Brin, and under the auspices of the company formed to develop and work the patents, and the process is now practical and economical, and is being worked on a large scale at various places.

The permanency of the baryta is mainly dependent on its physical condition, the use of reduced pressure during deoxidation, and consequent avoidance of excessively high temperatures, and the careful purification of the air used. It has been found possible to dispense with change of temperature in the reaction, change of pressure being now alone trusted to for determining the respective phases of oxidation and deoxidation. Neither the oxidation nor the deoxidation is as complete as when two temperatures were used, and the yield per operation is much less. But the duration of the operation is reduced from about 4 hours to 8–15 minutes, and the total daily yield is therefore largely increased. At the same time the operation is much simplified, the wear and tear of furnace, retorts, &c., very greatly reduced, and the fuel required lessened. Labour is also economised, the multiplied reversals of cocks &c. necessitated by the single-temperature method of working being effected automatically by reversing gear designed by K. S. Murray. The labour required is therefore little more than that needed for stoking the furnaces, and oiling and supervising the pumps &c.

The accompanying diagrams will explain the process as now worked. Fig. 1 shows the general arrangement of purifiers, pumps, and automatic gear; fig. 2 shows a transverse section and front elevation of the producer; fig. 3 a section taken at right angles to the front through the centre of the carbonic oxide generator and combustion chamber. The retorts R are suspended by flanges resting on the cast-iron top-plate P of the heating chamber, the lower ends passing out through holes in the base plate, lightly packed with asbestos to allow free expansion downwards.

'Producer gas' (carbonic oxide and nitrogen) is generated in G (figs. 2 and 3), which is fed with coke through F, the primary air supply entering by restricted openings at D. The producer gas passes through the opening A at the top of chamber G into the combustion chamber B, being met at its entrance by the secondary air supply, which, admitted at the inlets Q, has been heated by passing through the hot walls of the generator, as shown by the channels marked Q. Complete combustion takes place in chamber B, and the hot products of combustion then pass by the outlet holes S, shown in plan in fig. 3, and in section in fig. 2, into the heating chambers C, placed on each side of the combustion chamber, and in which the retorts are hung, and finally passes away at the bottom to the chimney.

Air is drawn in at the '*air intake*' (fig. 1) through a cock in the automatic gear G (fig. 1) by the pump P, by which it is forced, under a pressure of about 10–15lbs. per square inch, through another cock in the gear to the purifiers U. These are so arranged that either one or both lime purifiers and one soda purifier are in operation. The air then passes again through the automatic gear by a two-way cock to pipe J, which takes it to the distributing valve X at the top of the furnace. Thence it passes by pipes Y, to the inside row of retorts in each heating chamber, through which it passes downwards, and thence, by the connecting pipes N, shown in fig. 2, upwards through the outer rows of retorts, the air, largely deprived of its oxygen, finally escaping by the automatic relief valve on W. Provision is made in the distributing valve X, whereby the direction of the air current is altered at each operation so as alternately to pass downwards through the outer rows of retorts and upwards through the inner. When the oxidation has gone on for the suitable time the automatic reversing gear shifts over the cocks, the purifiers being cut out

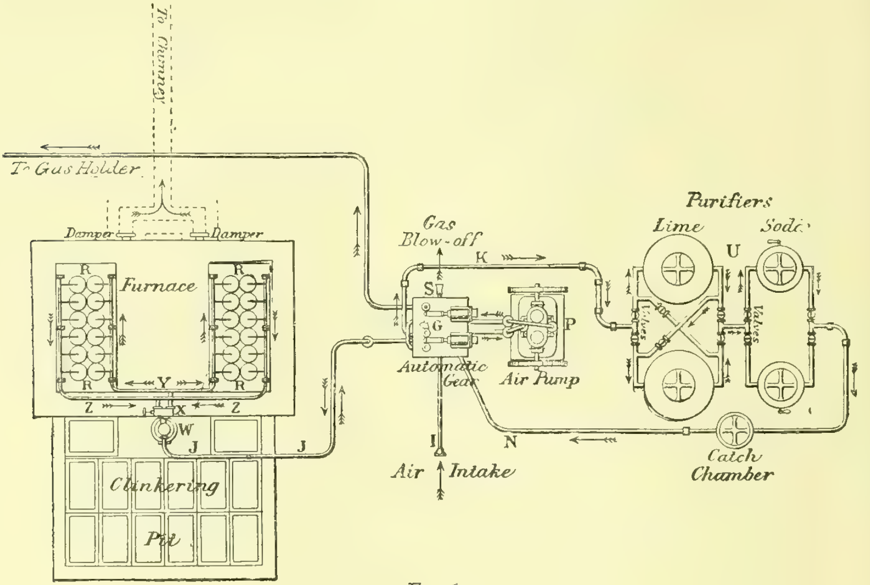


Fig. 1.

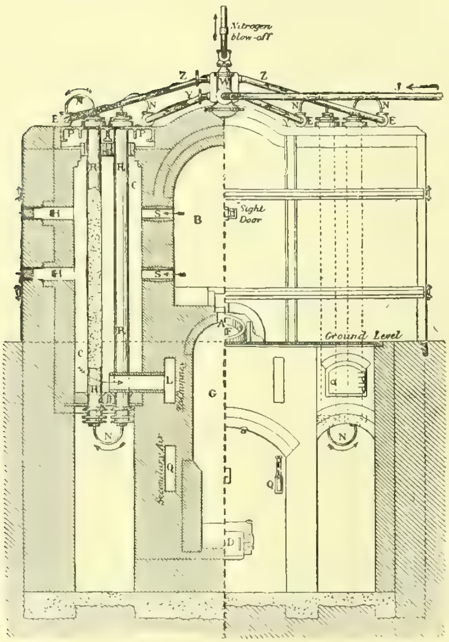


Fig. 2.

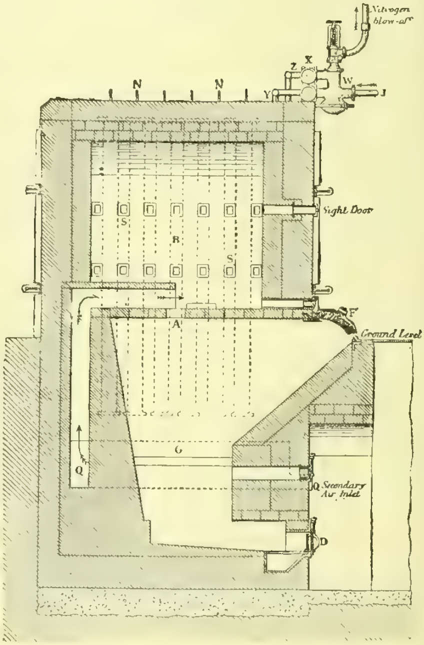


Fig. 3.

under pressure, and the exhaust cylinders of the pump brought into direct communication with the retorts through the distributing box X. A reduction of pressure is thus immediately caused, whereby the relief valve is automatically closed and the pipes Y and Z brought into communication with pipe J. As soon as the reduction of pressure in the retorts reaches about 26–28 ins. mercury (13–14 lbs. on the sq. inch) below that of the atmosphere the barium peroxide begins to give off oxygen. This is then drawn to the pump which delivers it into the holder. As the first portions of oxygen so drawn into the pump still contain much nitrogen, the automatic gear is arranged not to open the cock to the holder till a few seconds after the reversing of the other cocks, the mixed oxygen and nitrogen meanwhile escaping by a snifting valve, S, opened by the gear for the purpose.

For a producer capable of delivering 10,000 cubic feet of oxygen per 24 hours the consumption of coke in the furnace is about 12–15 cwt. per day, and for plant of that or smaller size the pump power required is about 1 I.H.P. per 1,000 feet of oxygen produced per day, the ratio decreasing for larger plants.

It is necessary that the barium oxide should be as hard and as porous as possible, and this is best obtained by preparing it by igniting the nitrate. The nitrate fuses and decomposition soon commences with evolution of a mixture of oxygen and oxides of nitrogen. This action continues for about 2 to 3 hours, during which time the contents of the crucible remain in ebullition. A porous mass is then left, which is heated for another hour to complete, as far as possible, the decomposition. In this way a very hard but also very porous baryta is obtained.

Under the present conditions of working, the baryta does not lose its absorptive power; but as there is a slight tendency to caking it is found advisable every six or seven months to remove the baryta from the retorts, break it up again and replace it, at the same time adding a little fresh in place of a small amount of dust formed by the friction of the air, &c. (K. S. Murray, Proc. I. Mech. E. 1890, 131; Thorne, S. C. I. 1890, 246).

Cost of production.—It is very difficult to obtain data of the cost of production of oxygen under the various methods described, but the following figures probably approximate pretty closely to the cost per 1,000 cubic feet:—from chlorate 8*l.*–10*l.*, from pyrolusite 4*l.*–6*l.*; from sulphuric acid 2*l.* 10*s.*–3*l.* (probably higher when only the oxygen and not the sulphur dioxide is utilised); by electrolysis (if the cost is proportionately divided between the hydrogen and oxygen formed) at least 25*s.*–30*s.*; and probably considerably higher; by the Tessié du Motay process 3*l.*–4*l.*; by the Brin process 3*s.*–7*s.* No authentic data of the cost of producing oxygen by dialysis or by solution in water are obtainable, but it would probably be *at least* as high as that by the Tessié du Motay process. In the Kassner process the cost depends largely on the amount realised by the sale of the caustic alkali. The process has not yet been tried on a large enough scale to yield trustworthy results as to cost; but the large amount of handling of material and consequently of labour required seems to preclude this being very low. In the various modifications of this process the cost would undoubtedly be lowered, but would still be prohibitive for technical uses.

Properties.—Oxygen is a colourless, tasteless and inodorous gas, of sp.gr. 1·1056 (air = 1): at 0°C. and 760 mm. pressure a litre of the gas weighs 1·43028 grams, and at 30 inches pressure and 15·5°C. 100 cubic inches weigh 34·206 grains. When examined through very thick and highly compressed layers, gaseous oxygen has a slightly blue tinge of colour. It is sparingly soluble in water. As with all gases, the quantity of oxygen dissolved by water depends on the tension of the oxygen in the atmosphere in contact with the water. Thus pure water shaken up in contact with pure oxygen will absorb nearly five times as much oxygen as it would when shaken up, at the same temperature and under the same pressure, with air—which only contains 20·9 p.c. by volume of oxygen. The following table gives the coefficients of solubility (*i.e.* the volume of oxygen absorbed by one volume of water when shaken up with pure oxygen under 760 mm. pressure) at different temperatures as determined by different observers:—

Temperature	Coefficient of solubility			
	Bunsen	Dittmar	Roscoe and Lunt	Winkler
0°C.	·0411	—	—	·0489
5°	·0363	—	—	·0429
10°	·0325	·0383	·0377	·0380
15°	·0299	·0344	·0339	·0341
20°	·0284	·0312	·0308	·0310
25°	—	·0286	·0284	·0284
30	—	—		·0262

These numbers multiplied by 1,000 give at once the number of c.c. oxygen absorbed by a litre of water from pure oxygen. The following table gives the number of c.c. of oxygen (calculated from the above table) absorbed by a litre of water from atmospheric air:—

Temperature	Oxygen absorbed by 1 litre water			
	Bunsen	Dittmar	Roscoe and Lunt	Winkler
0	8·60 c.c.	—	—	10·19
5°	7·58	—	–	8·91
10	6·79	8·00	7·87	7·87
15°	6·25	7·20	7·09	7·04
20°	5·93	6·53	6·49	6·36
25°	–	5·97	5 94	5·78
30°	—	—	—	5·25

The older numbers of Bunsen appear, from the results of more recent observers with more delicate apparatus, to be rather too low. Winkler gives the following formula for calculating the coefficient of solubility (β) of oxygen in water at any temperature (t).

$$\beta = \cdot 04890 - \cdot 0013413t + \cdot 0000283t^2 - \cdot 0000029534t^3.$$

The coefficient of solubility of oxygen in alcohol at 0° is 0·2337; at 20° it is 0·2201 (Timofejeff), so that oxygen is much more soluble in alcohol than in water.

Nearly all natural waters contain oxygen in solution, and can only be freed therefrom by prolonged boiling *in vacuo.* This dissolved oxygen, though small in amount, is the source from which fish obtain the oxygen necessary to sustain life.

Oxygen, though long regarded as a permanent gas, was liquefied in 1877 by Pictet at a pressure of 320 atmospheres, and a temperature of −140°. He attributed to liquid oxygen a density near that of water—about ·9787. More recently Wroblewski and Olszewski have worked, both conjointly and independently, on this subject, and have shown that the *critical temperature* of oxygen (*i.e.* the temperature above which no amount of pressure will liquefy it) is −113°, the pressure needed to liquefy it at that temperature being 50 atmospheres. The following table gives the vapour tensions of oxygen at varying temperatures (*i.e.* the pressure necessary for liquefaction at these temperatures) found by Wroblewski and Olszewski:—

t	Vapour tension	Density	Observer
−118°C.	50 atmospheres	—	W.
−123·7°	43·5 ,,	—	W.
−129·75°	—	·755	O.
−130°	—	·89-·90	W.
−131·6°	26·5 ,,	—	W. & O.
−133·4°	24·8 ,,	—	W. & O.
−134·43°	—	·806	O.
−135·8°	22·5 ,,	—	W. & O.
−139·3°	—	·877	O.
−145°	16·37 ,,	—	W.
−181·4°	742·1 mm. Hg	1·124	O.
−181·5°	740 ,, ,,	—	W.
−200·4°	20 ,, ,,	—	W.
−211·5°	9 ,, ,,	—	O.

Liquid oxygen is a pale steel-blue transparent and very mobile liquid (Dewar; Olszewski) boiling at −181·4 at ordinary pressures. When the pressure is reduced or removed, evaporation takes place so rapidly that a part of the oxygen is often frozen to a white solid. Thus under 13·7 atmospheres solidification takes place at −146·8, under 9 mm. Hg pressure at −211·5° (W.). This latter temperature is therefore pretty nearly the lowest obtainable by the evaporation of liquid oxygen. Liquid oxygen is a very perfect insulator, and is also comparatively inert in its chemical properties. Phosphorus, potassium, sodium, &c., may be immersed in it without any action taking place (Dewar).

Oxygen is the least refractive of all gases; it is slightly magnetic, but its susceptibility in this respect is diminished or temporarily suspended by elevation of temperature. Oxygen gives a characteristic though not very strong absorption spectrum, but to obtain this it is necessary to view the source of light through very great thicknesses of oxygen or through the highly compressed gas. The spectrum first appears in the form of a number of fine lines, but as the pressure is greatly increased or a layer of liquid oxygen is employed it shows a number of broader and shaded dark bands, with almost complete absorption in the violet. Six absorption bands have been observed, two in the red corresponding to the A and B Fraunhofer lines.

The chemical activity of air depends upon the oxygen it contains, air being simply, in its chemical relations, oxygen diluted with nitrogen. Free oxygen, whether diluted with nitrogen or not, manifests considerable chemical activity, even at ordinary temperatures, this activity increasing with rise of temperature. There are only seven elements—viz., fluorine, chlorine, bromine, iodine, silver, gold, and platinum—which do not unite directly with oxygen. All the non-metallic elements, with two exceptions, unite with oxygen to form anhydrous acids. Of the exceptions hydrogen forms a neutral oxide (water) whilst no oxide of fluorine has yet been obtained.

Phosphorus combines with oxygen at ordinary temperatures, as do also moist iron, moist lead, moist saw-dust, and many metallic compounds such as cuprous chloride, manganous hydrate, ferrous hydrate, &c. Potassium and sodium are at once attacked by dry oxygen at ordinary temperatures, becoming coated with their respective oxides. The majority of metals remain bright under similar conditions, but many become oxidised when moisture is present, though with many metals (for instance, iron) the presence of a trace of carbonic acid as well as moisture is essential to oxidation at ordinary temperatures. In some of the metals oxidised by exposure to air the first coating of oxide formed acts as a protective covering and prevents further oxidation, as is the case with lead. In others, however, the oxide first formed gradually becomes converted into a higher oxide and may then give up part of its oxygen to the metal in contact with it, and the oxidation is thus propagated through the mass of the metal. The rusting of iron is not a simple case of oxidation. The combined action of moisture, carbonic acid, and oxygen appears to first form an hydrated ferrous carbonate. This is then decomposed by the absorption of more oxygen, being converted into an hydrated ferric oxide, the carbonic acid being again liberated. Some water appears also always to be decomposed during the formation of iron rust, hydrogen being liberated in traces (*v.* Rust). Some metals which in their ordinary condition are comparatively inert towards oxygen combine with it readily at ordinary temperatures when they are in a finely divided state, offering a very large surface for chemical action. Thus lead or antimony when obtained by the ignition of their tartrates, and iron, nickel, cobalt and copper, when reduced from their precipitated oxides in a current of hydrogen at a low temperature, all ignite spontaneously when poured into air or oxygen, and when in this finely divided state are therefore often termed *pyrophori.* Silver, gold, and platinum are not acted on directly by oxygen at any temperature.

The activity of oxygen is increased greatly by increase of temperature, and with most substances (except under the conditions already mentioned) an initial heating is necessary to start free oxidation, the heat evolved during oxidation being then sufficient to maintain it.

Thus iron heated to bright redness in an atmosphere or stream of oxygen takes fire and burns brightly. A mixture of oxygen and hydrogen may be kept at ordinary temperatures for any length of time without change, but if the temperature of any part of the mixture be raised to bright redness—either by the electric spark, by the presentation of a flame or by other means—ignition at once takes place with explosive force throughout the whole mass. Under certain circumstances, however, this combination may be effected at ordinary temperatures. Thus, if a piece of clean platinum foil be hung in the mixture, combination takes place gradually at ordinary temperatures. This appears to be due to the power possessed by palladium, platinum, and some other substances of condensing gases and especially hydrogen on their surfaces, the activity of the so condensed gases being thereby greatly increased. If platinum or palladium black or sponge is used instead of foil, the action is so much increased that the heat evolved in the combination soon raises the temperature of the metal to the ignition point, and ordinary combustion ensues. This effect has been taken advantage of in the *Döbereiner* lamp (named after the investigator who first noticed this property of platinum) wherein a piece of spongy platinum is suspended over a jet connected with an automatic hydrogen-generating vessel. When the tap of the jet is turned on, the jet of hydrogen becoming mixed with air and at the same time impinging on the spongy platinum, oxidation takes place rapidly, the platinum soon becomes red hot and ignites the jet of hydrogen. Similar effects are produced with oxygen (or air) and hydrocarbon gases.

Various substances which expose large surfaces to air (or oxygen) become gradually heated through slow oxidation or combustion, and, if the heat cannot get away, ignition eventually occurs. Thus oily or greasy woollen and cotton rags and refuse are capable of absorbing oxygen pretty rapidly, and if present in any quantity the heat produced may accumulate and cause spontaneous combustion, and this action is a not infrequent cause of fires in factories. A similar generation of heat and eventual 'spontaneous combustion' often arises from the storing of moist hay in hayricks, and from the storage of damp coal in ships or heaps. The allegation that the ignition of coal is due to the oxidation of pyrites has been disproved by the work of Richters and Lewes, who have shown that the heat is generated by the absorption of oxygen and its action on the bituminous constituents of the coal.

Dixon, Baker, Traube, and others have recently shown that even at high temperatures the presence of a trace of moisture is necessary for free oxidation (combustion), and that in *absolutely* dry oxygen, sulphur and phosphorus can be distilled, and carbon made red-hot without combustion taking place. A jet of burning dry carbonic oxide is even extinguished when introduced into pure and absolutely dry oxygen. The presence of the minutest trace of moisture is, however, sufficient to restore to oxygen its well-known activity.

In ordinarily dry oxygen all substances which burn in air burn with much greater brilliancy, and many substances which do not burn in air burn vividly in oxygen. Thus iron, zinc, &c., if the ignition is started by a portion being raised to a white heat in an atmosphere of oxygen continue to burn with great brilliancy and with the evolution of a very high temperature. The actual amount of heat given out during the complete oxidation of any substance is the same whether the combustion is slow or rapid, and is carried on in air or in oxygen. But it is quite different in regard to the temperature developed, this depending on the concentration of the heat, and so being higher the more rapid the combustion and the less extraneous matter is present to absorb the heat. Thus, when phosphorus is burned in oxygen, the temperature produced is very high, and the combustion takes place with dazzling brilliancy. The temperature of a hydrogen or a coal-gas flame burning in oxygen is very much higher than that of a similar flame burning in air. This fact has been utilised in the construction of the oxy-hydrogen blowpipe for obtaining very high temperatures. If coal-gas is substituted for the hydrogen, a very hot flame is still obtained, but the temperature is not as great as when hydrogen is employed. Besides being much hotter, the oxy-hydrogen and oxy-coal-gas blowpipe flames are much smaller than the corresponding air blowpipe flames, and the heat can therefore be better localised.

Oxygen is the only gas capable of supporting respiration, and forms the life-maintaining constituent of air. In the pure state it may be inhaled for a time with impunity, and acts as a mild tonic or exhilarant. But its long-continued respiration is harmful, feverishness and weakness being produced; and it becomes poisonous if breathed under pressure. Dr. Richardson kept a rabbit in an atmosphere of pure oxygen at a temperature of 23·9°C. for three weeks. It ate voraciously all the time, but became so emaciated from inability to assimilate new material fast enough to supply waste that it was found necessary to discontinue the experiment. At 7·2°C. the rabbit became speedily narcotised, and would have died had it not been removed. Richardson found that cold-blooded animals were very little affected by being introduced into an atmosphere of oxygen, whilst most warm-blooded animals (dogs, cats, guinea-pigs, &c., but not the rabbit) speedily showed strong febrile symptoms (Asclepiad 1887–89). Some observers have noticed very decided narcotic effects produced on animals under these conditions, but Richardson ascertained that this is due to the oxygen becoming vitiated by repeated inhalations. He found that when the same oxygen was used over and over again, although purified from carbonic acid, &c., by passage over caustic potash, sulphuric acid, &c., the animals became speedily narcotised, but that when a continuous stream of fresh oxygen was employed this was not the case. This 'de-vitalising' of the oxygen appears to be due to traces in the exhaled gases of some compound which is not removed by the ordinary methods of purification. The electric discharge very quickly re-vitalised the vitiated oxygen. Flesh was found to decompose more readily in devitalised than in pure oxygen. At low temperatures, and at very high ones, however, oxygen is decidedly narcotic in its effect.

But though in health the continued inhalation of nearly pure oxygen is detrimental, its use where the action of the lungs and heart is sluggish, as in cases of partial suffocation, of collapse in cholera and other illnesses, is very valuable, and has been the means of saving many lives. Its use in cases of cyanosis, gout, diabetes, and so on has also been found advantageous.

Methods of testing and estimation.—The readiest test is the property possessed by oxygen of moderate purity of re-kindling a glowing splint of wood, a property only possessed by one other gas—viz., nitrous oxide. When mixed with colourless nitric oxide gas, oxygen produces deep reddish-brown fumes of nitric peroxide, whilst nitrous oxide does not. Nitrous oxide is also much more soluble in water than oxygen.

White indigo absorbs oxygen rapidly, at the same time turning blue. For general purposes of estimation, however, one of the three following methods is generally used:—

1. A solution of cuprous chloride in hydrochloric acid (which is colourless) absorbs oxygen readily with formation of cupric oxy-chloride. The greenish-brown solution of this salt may be again reduced by keeping copper foil in it.

2. An alkaline solution of pyrogallic acid absorbs oxygen freely, forming a dark-brown liquid. The best results are obtained by mixing 45 c.c. of a 25 p.c. solution of pyrogallic acid (prepared by dissolving 60 grams acid in 180 c.c. water) with 145 c.c. of 60 p.c. solution of caustic potash (prepared by dissolving 400 grams ordinary stick potash in 300 c.c. water). 200 c.c. of this solution will absorb nearly two litres of oxygen, but it is better not to push the absorption to its full extent, as the rate of absorption becomes at last very slow.

3. Clean moist copper absorbs oxygen freely, but a skin of sub-oxide is rapidly formed over the copper, which prevents further oxidation. An ammoniacal solution of ammonium carbonate, however, readily dissolves this sub-oxide again, leaving the clean copper. To utilise this reaction for analysis a suitable absorption vessel is packed with fine copper wire and then filled with a solution composed of equal volumes of ammonia of sp. gr. ·930, and of a saturated solution of commercial ammonium carbonate. When the gas in which the oxygen is to be estimated is introduced into the vessel and displaces the liquid, a large surface of clean copper is exposed, and the oxygen is rapidly absorbed. When the residual gas is removed, the liquid again fills the vessel and dissolves the sub-oxide of copper formed, leaving the copper clean for the next analysis. 200 c.c. of this solution will dissolve the oxide formed by the absorption of about four litres of oxygen, but it is advisable to renew it after the absorption of about three litres, as otherwise a good deal of a yellowish-brown precipitate (probably an ammonio-copper compound) forms which renders the renewal more troublesome. A little fresh copper wire must be occasionally added as that in the vessel gets used up.

For all these tests Hempel's, Orsat's, or Stead's apparatus (see Analysis) answer well for all but the most delicate determinations. With these an oxygen determination can easily be made in ten minutes.

If the first method is employed, the gas after absorption must be freed from hydrochloric acid by means of potash. In the second there is a liability under certain conditions to the formation of traces of carbonic oxide during the action of the alkaline pyrogallate, but the quantity is always very small.

The property of phosphorus of absorbing oxygen at ordinary temperatures is also sometimes used for analytical purposes, but this is not a generally convenient method.

Applications of oxygen.—Oxygen has been used successfully to maintain the air in a respirable condition in places where it cannot be replaced, as in diving-bells, submarine vessels, &c. Its use has often been suggested in connection with the ventilation of large halls, theatres, &c., but the cost has hitherto proved too great for its adoption.

It is employed in conjunction with hydrogen or coal gas to produce the oxy-hydrogen and oxy-coal-gas flames in which platinum can be melted, silver distilled, &c. One application of these flames is in the production of the Drummond or lime light where the intense heat of the flame is made use of to raise a lime cylinder to a white heat and thus obtain an intensely vivid source of light. The oxyhydrogen and oxy-coal gas blowpipe is also used for the brazing of metals, autogenous soldering, the blowing and manipulation of hard-glass apparatus, and for many other purposes where very high temperatures and local heating are required.

Oxygen is used for many purposes in the laboratory, and, as already mentioned, for some medical purposes. It has been found that the admixture of small proportions (up to 6 or 7 p.c.) of oxygen with nitrous oxide during anæsthetising with that substance prevents or reduces the tendency to convulsions experienced with pure nitrous oxide, without reducing appreciably its anæsthetic power. Johnson has shown (Pr. 49, 148) that anæsthesia may be produced with nitrogen equally as well as with nitrous oxide, and that a mixture of nitrogen with 5–7 p.c. oxygen forms a very satisfactory anæsthetic, producing slight or no convulsions.

Oxygen has recently been applied in the purification of coal-gas from sulphur compounds. It is found that if from ·5–1 p.c. of oxygen is added to the crude coal-gas before it enters the purifiers the reduction of the sulphur compounds to 8–12 grains per 100 cubic feet of gas may be effected by lime alone, the use of oxide of iron or lime sulphide being unnecessary. If oxide of iron is used, its efficiency is increased. In any case the purifying space needed is lessened, the life of the purifying material is lengthened, and the luminosity of the purified gas is considerably increased. If lime is used for purification the fouled lime ('blue billy') has not the objectionable odour which it usually possesses (Valon, Trans. Gas Inst., 1889, p. 41).

It has been found that if, during the bleaching of paper pulps with bleaching powder, oxygen in a fine state of division is introduced into the bleaching potcher, a great saving of bleaching powder is effected, the bleached fibre also being stronger in texture (Thorne, S. C. I. 1889, p. 83).

Pure oxygen is also advantageously employed in the oxidation and thickening of oils for varnish and linoleum purposes. The thickened oil is paler in colour than boiled oil, the danger is less, as only steam heat is needed, and the thickening, besides being much more rapid, is accompanied by increase of weight instead of by loss of weight as in the ordinary process of boiling. The use of driers is also unnecessary (Eng. Pat. 18,628, 1889).

Oxygen is now sometimes used to hasten the maturing of spirits, the same effect being produced in a few hours or days by means of pure oxygen acting on the spirit in a finely divided state as occurs under the ordinary method of storage in casks in two or three years.

Proposals have recently been made to use a mixture of oil gas and oxygen as an illuminating gas (Tatham, Eng. Pats. 1889, Nos. 13,763, 16,138, and 16,142). It is found that, if 15–30 p.c. of oxygen is added to an oil gas retorted at a low temperature from a heavy and crude petroleum, a gas of very high illuminating power and of good travelling properties is obtained. The gas is a perfectly safe gas, as about its own volume of oxygen must be added to a heavy oil gas before an explosive mixture is formed. The same inventor proposes (*l.c.*) to use carburetted oxygen as a motive gas for engines, &c. He claims that with properly constructed valves, &c., perfect safety is secured, and that the great expansive force of carburetted oxygen on ignition gives results far superior to those obtained in the ordinary steam or gas engine.

The use in the manufacture of vinegar of small quantities of oxygen to act as a stimulant on the mycoderma has been recently found to considerably increase the rate of acetification.

L. T. T.

OXYNARCOTINE *v.* Vegeto-alkaloids.

OXYTOLUENES *v.* Cresol.

OZOKERITE. A naturally occurring solid hydrocarbon of the olefine, or C_nH_{2n} series. According to Grabowski, ozokerite is found chiefly in the Miocene formation at Boryslaw, near Drohowycz, and in the region of Stanislawow, Galicia. The veins in which it occurs are 40 to 80 mètres deep, and 1 mètre in diameter. They pass through beds of sand, from 8 to 10 mètres deep, containing large stones, and then through blue clay and a plastic loam. From this blue clay, naphtha usually springs. The centre of the basin is richest in wax; in some cases masses of such extent have been tapped that the miners have hardly had time to escape before the workings were filled with the plastic mineral. Such a deposit was recently found in the deepest shaft at Boryslaw, at a depth of 208 metres (227 yards). In general, however, the yield of wax varies at from 2 to 8 p.c. of the mineral extracted. Ozokerite was first found in this district in 1854 by Doms, who was in search of petroleum, with which much of the ground is saturated. At first it was regarded as an unwelcome companion to the petroleum, as it frequently caused the timbering of the shafts to collapse. It was not until about twenty years later that this substance began to attain commercial importance, a method having then been discovered of producing from it a substance resembling beeswax and named ceresin.

In 1865 ozokerite, which had previously been regarded as a Crown mineral, was declared free, and the consequence was that a number of shafts were sunk in the district, and much speculation ensued. The land being parcelled out in small plots, the shafts were sunk in the immediate neighbourhood of each other, and much waste and danger ensued. In 1886 the present law was passed, according to which the right of mining for ozokerite may be separated from the ownership of the land. The extraction is now carried out under official supervision. In nearly every case the mineral is raised through vertical shafts or pits over which a wooden roof is erected. The section of the shafts in the first instance is 3 to 4 square mètres (32 square feet to 43 square feet); but, when the ozokerite formation is reached, an inner shaft 1 mètre square (10·76 square feet) is formed of timber, and the space between this and the timbering of the larger shaft is filled with a rich clay. This construction is adopted to exclude the surface-water, which is kept down by hand-pumps during the sinking. From the bottom of the shafts levels are driven into the ozokerite ground, the richer portions being raised and the refuse used to fill up the old workings. The softer parts of the marl are dislodged by means of pick or wedge; but where the rock is hard, and the permission of the mining authorities can be obtained, dynamite is used. The mineral is raised by hand in skips or tubs holding 40 to 50 kilos. (88 to 110 lbs.). Hand-ventilators are used for the purpose of ventilation, but explosions of gas are not uncommon, especially after Sundays and holidays. The mortality from accidents is about 2 p.c. per annum. Safety-lamps (Mueseler or Marsaut) are used in all the mines. The timbering of the shafts requires constant renewal and repairs; in some cases it is almost impossible to keep the shafts perpendicular.

The water is usually raised in tubs, and much difficulty is experienced in getting rid of it after it reaches the surface, on account of the numerous shafts and the broken nature of the ground. The mineral, when it leaves the tubs, is sorted by hand. The waste rock is picked out and tipped to spoil, lumps of ozokerite are specially selected, and the remainder of the rock, containing fragments of wax, is tipped into tanks full of water. On being well stirred, most of the wax rises to the surface and is skimmed off. The residue still contains from 2 to 3 per cent. of wax. The quantity of waste mineral being considerable, and the distance between the shafts small, a special railway has been built to remove the residues from the immediate neighbourhood of the mines.

Only one attempt has been made to mine on a large scale for ozokerite. In this case a circular shaft, 2 mètres (6 feet 7 inches) in diameter, and lined with iron tubbing, was sunk outside the ozokerite zone, and the deposit was reached by galleries. Trucks holding 500 kilos. (1,102 lbs.) were used, and both ventilation and pumping were done by steam-power. The operations on a large scale do not, however, seem to have been successful, the French company which carried them out having now ceased working.

The annual production has varied from 4,000 to 18,000 tons, and in certain years the value has exceeded 1,800,000 dollars.

Other deposits of ozokerite are found at Truskawice, Starunia, and Droniacz, always in Miocene formations.

The production of ozokerite in the Boryslaw district amounted, in 1887, to 96 p.c. of the total output in Galicia, and was valued at 152,900*l*. (J. Shotsky, Allg. österr. Chemiker- und Techniker-Zeit. 1889, 614, 651; S. C. I. 9, 597).

The ozokerite forms lumps and layers from 3 to 9 decimètres thick, so that masses are often found about 100 kilos. in weight. The native ozokerite is transparent, of a light-yellow colour, and of the hardness of beeswax. The best ozokerite is yellow or greenish, and can be easily compressed between the fingers. This kind, however, is not much used for the preparation of cerasin. The composition of ozokerite may be best represented by the formula C_nH_{2n}. It appears to have been formed by the oxidation and decomposition of the hydrocarbons of naphtha, since the action of oxygen on these compounds simply eliminates hydrogen. Thus, for example, naphthalene gives dinaphthyl and water: $2C_{10}H_8 + O = C_{20}H_{14} + H_2O$. By further oxidation compounds are obtained of the formula C_nH_{2n}, which react with the hydrocarbons of the marsh-gas series, with formation of very complex carbon compounds of various melting-points, as for example:—

$$2C_8H_{18} + O_2 = C_{16}H_{32} + 2H_2O, \text{ and}$$
$$C_{16}H_{32} + C_8H_{18} + O = C_{24}H_{48} + H_2O.$$

According to this hypothesis, the formation of cerasin from naphtha by the oxidation of the compounds of the marsh-gas series, and the relationships of ozokerite, naphtha, and coal, can be explained in the simplest manner. The best kinds of ozokerite are used in the preparation of cerasin, all foreign matters being eliminated by means of sulphuric acid and animal charcoal. Good cerasin is not easily distinguishable from beeswax. The following are the best methods of discrimination—(1) Cerasin is not so easily kneaded between the fingers as beeswax, and is more brittle. A mixture of the two bodies cannot be recognised in this way. (2) Cerasin is almost unacted on by concentrated sulphuric acid, whilst beeswax undergoes perfect decomposition by such treatment (S. C. I. 11, 473).

Ozokerite is known to be found in the Caucasus, and there are reports of its occurrence among the Wasatch Mountains, Utah, about 173 miles east of Salt Lake City, America, where deposits of white ozokerite, miles in length, are said to be found.

Lach, having had samples of the Caucasian ozokerite submitted to him, has examined them by his process (Chem. Zeit. 9, 905; S. C. I. 1885, 488), with the following results:—

Caucasian ozokerite resembles an inferior Galician variety. Melting-point of crude substance 68°C. Treated with 20 p.c. of fuming sulphuric acid it yields 58·1 p.c. of second-quality cerasin; m.p. 68·5°C.; volatile portion, 1·8 p.c. The crude substance has a repulsive odour, is worked with difficulty in quantity, becomes stiff in the basin, and presses extremely badly. The price is at present too high, and until greater demand arises and the transportation is facilitated, the Galician ozokerite production will make very strong competition.

North American or Colorado ozokerite. Here extensive deposits of an ozokerite-like substance are found, the supply from which is hindered only by the transport difficulty. On being tested, however, the material seems to be of little use for the production of cerasin. It is supplied in cakes 36 × 20 × 6 cm. in dimensions. It is a dull black, hard substance, brittle and pulverisable, and smelling of catechu. Care must be taken in heating it, as violent frothing may occur from the presence of water.

The crude substance melts at 76·0°C.

Treated by the aforementioned process no cerasin is obtained. Even when heated to 300°C. it is impossible to filter it, although it is quite a thin fluid. Subjected to distillation it gives the following results:

	Per cent.
Paraffin oil . . .	90·00
Gas	2·12
Water	2·60
Residue	5·28

It commences to distil at 360°C., when nearly 3 p.c. of oil, solidifying at 30°C., comes over. At a much higher temperature it distils steadily, giving a very fair crude product for paraffin extraction. This substance is apparently more suitable for paraffin-making than for the cerasin industry (B. Lach, Chem. Zeit. 13831; S. C. I. 8, 696).

OZONE, or *Active oxygen*. Symbol O_3; molecular weight, 47·88. Van Marum, in 1785, noticed that air or oxygen in the neighbourhood of an electrical machine, or through which a series of electric sparks had been passed, acquired a peculiar odour, somewhat resembling that of chlorine; and Cruickshank, in 1801, noticed a similar smell during the electrolysis of water. But Schönbein, in 1840, was the first to recognise that this smell was due to the formation of a new gas, to which he gave the name ozone (ὄζω, to smell). Shortly afterwards he found that ozone was also formed by the action of moist air on phosphorus. At first this substance was considered to be an oxide of hydrogen, but the researches of Marignac and De la Rive, of Andrews and Tait, of Fremy and Becquerel, of Brodie, and others, and especially of Soret, established the fact that ozone is an allotropic form of oxygen produced by the condensation of three volumes of oxygen into two of ozone; or, in other words, that, whilst the molecule of oxygen contains two atoms, that of ozone contains three. Its formation may be expressed by the equation $3O_2 = 2O_3$. One view held for some time was that ordinary oxygen was composed of negative oxygen, or *ozone*, and positive oxygen, or *antozone*, but the existence of the third form, or *antozone*, has been disproved.

As already stated, ozone is formed when a series of electric sparks is passed through oxygen or air, but the proportion of the oxygen so transformed is very small. A much larger proportion of ozone is formed when the silent discharge is substituted for the spark discharge.

For this purpose a slow current of air or oxygen is passed between the terminals of an induction coil placed at a short distance apart and made as large in area as possible. The Siemens 'induction tube' consists of an inner tube, which is either of metal, or, if of glass, is lined or covered with tinfoil, and a rather larger outer tube, which is covered with tinfoil. A current of air or oxygen is passed through the narrow annular space between the tubes, the metallic surfaces of the inner and outer tubes being connected with the terminals of an induction coil or electrical machine, and thus transformed into terminals of large area. A better result is said to be obtained when no glass intervenes between the terminals. A number of modifications of this apparatus have been suggested—in some of these the metallic terminals are replaced by good conducting solutions, such as copper sulphate solution, &c., in others by shot, powdered graphite, &c.—but in all the principle is the same, viz., the passage of a current of oxygen between terminals of large area, placed very close together, and thus offering as little resistance as possible to the silent discharge and reducing sparking to a minimum.

More ozone is obtained when a current of oxygen is used than when air is employed. The proportion is also increased by thoroughly drying and cooling the oxygen, by increasing the pressure, and by bringing the terminals as near together as possible. Sparking is very detrimental, destroying much of the ozone formed. The best result appears to be obtained when there is a continuous 'glow' discharge. If the air is moist, some nitric acid is almost invariably formed. Under the most favourable conditions, and when great care is taken to keep the temperature of the apparatus and gas low, about 25 p.c. of the oxygen may be converted into ozone; but ordinarily, or on the large scale, the proportion obtained is much smaller.

Leeds, using a battery of six induction tubes excited by a twelve-cell galvanic battery and Ruhmkorff coil, giving a 45-inch spark, obtained on an average 2 litres of ozonised oxygen, containing 5 p.c. ozone per hour. The ozonisers were placed in a refrigerating chamber and surrounded by dry air at 0° (C. N. 40, 249).

Ozone may be obtained in small quantities by putting a few pieces of clean phosphorus in a bottle containing oxygen or air and a little water. In about an hour the smell of ozone will be obvious, and the phosphorus should then be removed, otherwise the ozone rapidly disappears; or a current of oxygen or air may be passed through one or more Woulff's bottles containing pieces of moist phosphorus, and finally through water. In this way slightly ozonised air or oxygen is obtained. This reaction does not take place at or below the freezing-point of water, nor unless moisture is present.

Ozone is produced in small quantities when a heated glass rod is plunged into a mixture of air and ether vapour.

The oxygen evolved during the electrolysis of strongly-acidulated water contains a small quantity of ozone, but this does not exceed $\frac{1}{250}$ of the evolved oxygen.

By the action of strong sulphuric acid on barium peroxide, oxygen containing a considerable quantity of ozone is given off.

Fluorine decomposes water, and this reaction is accompanied by the formation of ozone (Moissan, C. R. 103, 202 and 256).

Ozone is produced in minute quantity during the evaporation of water, especially when the latter is in the form of spray. This probably is one source of the ozone present in sea air.

Many organic substances, such as turpentine, some of the essential oils, pieces of apple, &c., have the property of producing small quantities of ozone when exposed to the air.

Properties.—Ozone is a gas having a characteristic and very strong odour somewhat resembling that of dilute chlorine. Ozone has never been obtained pure in the gaseous form, always being diluted with oxygen. When ozonised oxygen is subjected to a pressure[1] of 125 atmospheres at the boiling-point of ethylene (−103°) ozone is condensed in the form of a deep-blue liquid, the superincumbent highly compressed gas being also of a deep-blue colour (Hautefeuille and Chappuis). Liquid ozone is also deposited when a slow current of ozonised oxygen is passed through a tube, cooled by being surrounded by boiling oxygen (−181°). When the pressure is removed, or the temperature allowed to rise, the liquid ozone evaporates to a blue gas. The boiling-point under atmospheric pressure is −106° (Olzewski). The blue colour is not generally apparent in ozonised oxygen, owing to the dilution by the oxygen. But, when viewed through a layer of a yard or more in depth, ozonised oxygen is seen to have a distinctly blue colour. It is possible that the blue colour of the sky is in part due to the ozone present in the atmosphere.

Very varying statements are made as to the solubility of ozone in water, some observers stating that it is insoluble. It is undoubtedly somewhat soluble, however, though the degree has not yet been satisfactorily determined. From some of the most trustworthy results it appears to be at least ten times as soluble in water as oxygen is. Thus Carius found the coefficient at 1° = ·834, Schöne at 18° = ·366, and McLeod at 14° = ·274. The solution acts as a powerful oxidiser, and has the characteristic odour of ozone. The ozone in solution gradually disappears, and simple agitation of ozonised oxygen with water destroys much of the ozone.

Ozonised oxygen, at ordinary temperatures, when dry and in vessels from which the air is excluded only slowly decomposes. At 100° the decomposition is somewhat more rapid, and at 260° it is instantaneous. Mulder finds—other conditions remaining the same—that the rate of decomposition of ozone in admixture with oxygen varies in proportion to the percentage of ozone, and increases rapidly with increase of temperature. Moist ozone is less stable than dry.

Ozone is a very strong oxidising agent, giving up one third (one atom) of its oxygen very readily. Thus it converts copper, mercury, silver, and iron into the corresponding oxides, but this reaction appears to require the presence of moisture. Ozone has a remarkable effect on mercury, one bubble of oxygen, containing $\frac{1}{50}$ of its bulk of ozone, being sufficient to alter the physical condition of several pounds of mercury. The mercury loses its mobility, convexity of surface and lustre, and adheres to the surface of glass. If the ozone is moist, permanent oxidation takes place, but if perfectly dry the mercury is said to recover its usual physical properties when exposed to dry air. Ozone oxidises most organic compounds, destroying caoutchouc and vulcanite, for instance, very rapidly, so that caoutchouc and vulcanite connections must be avoided in its preparation. It oxidises sulphide of lead to sulphate, ferrocyanides to ferricyanides, manganous to manganic compounds, and so on. Dry ozone is absorbed by dry mercury and dry iodine. Ozone bleaches many vegetable and animal colouring matters, such as indigo, litmus, blood, &c.

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[1] During compression care must be taken to keep the temperature from rising much, as otherwise during rapid compression the ozone is liable to explode with great violence.

Dry ozone is decomposed in unlimited quantity by the peroxides of manganese and lead, by black oxide of copper, and also by dry silver leaf, the oxides or silver undergoing no permanent change. These effects are probably due to the successive or simultaneous formation and decomposition of higher oxides. In the case of silver leaf the alternating formation and decomposition of silver oxide may be observed. In some cases ozone acts, like hydrogen peroxide, as a deoxidising agent on highly oxidised compounds. Thus hydrogen peroxide is reduced to water, and barium peroxide to the monoxide. In these cases the ozone is simultaneously decomposed: $O_3 + H_2O_2 = 2O_2 + H_2O$. Ozone is also decomposed when agitated with powdered glass, or by passage over spongy platinum or palladium. It is, however, without action on permanganic or perchromic acids.

Moist ozone oxidises phosphorus, sulphur, selenium, tellurium, and arsenic to phosphoric, sulphuric, selenic, telluric, and arsenic acids, ammonia to nitrous and nitric acids, and silver and lead to their peroxides. It liberates iodine from potassium iodide, the potassium being converted into the hydrate $2KI + O_3 + H_2O = 2KOH + O_2 + I$. This reaction forms one of the best means of determining the amount of ozone in a gas, as the iodine liberated can readily be estimated by titration.

In all the above oxidations the volume of the gas remains unaltered, the molecule of ozone giving up one atom of oxygen to the substance and leaving a molecule of oxygen: $Cu + O_3 = CuO + O_2$. Turpentine and many essential oils, however, absorb the ozone molecule as a whole, and the reaction has been utilised to determine the composition of ozone. Thus, if a carefully measured quantity of dry oxygen is ozonised, the contraction carefully noted, and then the resultant gas shaken with turpentine, the ozone is absorbed with a further contraction, twice as great as the first, the remaining gas being oxygen. This points to the contraction of three volumes of oxygen to form two of ozone, and this result has been confirmed by Soret, who determined the relative rates of diffusion of mixtures of ozone and oxygen and of chlorine and oxygen. The molecule of ozone, therefore, contains three atoms of oxygen, one of which is easily liberated in the nascent state, and so forms a powerful oxidiser, $O_3 = O_2 + O$.

The great chemical activity of ozone is probably due to the fact that it is an endothermic compound, and thus gives out a considerable amount of heat when it decomposes. The heat of formation of ozone (48 grams) from oxygen has been determined by several chemists. Berthelot's results gave −29·6 cals., Van Meulen's −32·6 cals. by oxidation of arsenious acid and −36·6 cals. by direct decomposition by platinum sponge.

Ozone gives an absorption spectrum consisting of numerous broad bands. From the comparison of the sun's spectrum, as seen at different periods of the day, with the ozone absorption spectrum, Hartley concludes that ozone is always present in the upper portions of the atmosphere.

Ozone is most readily detected by means of paper moistened with a mixture of starch and potassium iodide. If ozone is present, iodine is liberated, and the starch paper coloured blue. This reaction, however, is also produced by nitrous and nitric acids, by chlorine, &c., so that it is not conclusive. A more conclusive test is to take a piece of neutral litmus paper and moisten half of it with a neutral solution of potassium iodide. If now this paper is subjected to the action of ozone the potassium iodide is oxidised and caustic potash formed, which at once turns the litmus paper blue. The turning blue of the part of the litmus paper not treated with the iodide would indicate the presence of any ammonia, which might otherwise be taken for ozone. Chlorine, nitrous acid, &c., if present, would form a neutral potassium salt, or would show an acid reaction. If, then, the untreated end remains the neutral purple whilst the iodised end turns blue, the presence of ozone is pretty conclusively proved. Papers moistened with guaiacum or with tetramethyleneparaphenyldiamine, both of which are turned blue by ozone, are very sensitive, but, like iodised starch paper, are also similarly acted on by other oxidising agents. For the quantitative determination of ozone the potassium iodide reaction is the best. If the presence of oxidising agents other than ozone is suspected, two estimations should be made, the one of the gas in question, the second after the gas has been passed through a tube, heated at 260° to destroy the ozone. The difference of the two tests gives the ozone present.

Ozone is present in minute quantities in the atmosphere. Its principal sources are probably the electric discharge during thunderstorms, the silent discharge from thunder-clouds, the evaporation of water, and especially of saline waters, as in the sea foam, and the action of some vegetable products on the air. Wurster found (B. 19, 3208) that ozone is also formed by the action of sunlight on clouds. When clouds are continually formed from above (*i.e.* in sunlight), all become laden with ozone, whilst when they are formed from below the upper layers are much more charged than the lower.

The ozone present in the atmosphere probably plays an important part in keeping the air pure and fresh and destroying the deleterious organic matter constantly passing into the atmosphere from decomposing flesh, animal exhalations, &c. In the open country, and especially by the seaside, ozone can always be detected, but in the air of large towns it is either absent or present n much smaller quantities. Richardson has proposed (Asclepiad, 1887) the artificial production of ozone for the purpose of purifying the air of sick-rooms and even of towns, suggesting the Wimshurst electrical machine as probably a suitable ozone generator for this purpose.

When present in the air in very minute quantities ozone appears to be very advantageous to health, but if the quantity present is enough to be readily detected by the odour it is found o have a very irritating and harmful effect on the mucous membrane and the system, producing headache, influenza, &c. If the quantity present is large it becomes a strong irritant poison. Slightly ozonised air and oxygen is now sometimes used medicinally, especially in pulmonary complaints.

Besides its medicinal uses, ozone has been employed, apparently with some success, for the rapid aging of spirits (Tieillard). It has also been utilised to oxidise alcohol to aldehyde and to vinegar, as a bleaching agent in the manufacture of stearine wax and other organic substances, but the present methods are still too costly to allow of its practical commercial application. It is used for bleaching discoloured engravings, &c., the engraving being rolled up and introduced into a glass vessel, in the bottom of which some water and pieces of phosphorus are placed. L. T. T.

P

PACHNOLITE (πάχνη, rime). A fluoride of aluminium, calcium, and sodium, occurring as an incrustation or efflorescence on cryolite. It s regarded by Knop as a hydrated cryolite in which two-thirds of the sodium are replaced by calcium (A. Knop, A. 127, 61; Wöhler, J. M. 1876).

Composition.—

Al.	Ca.	Na.	F.	H_2O.
13·43	17·84	10·75	49·78	8·20 = 100·00

PACKFONG or **PACKTONG**. A Chinese alloy resembling nickel silver, and of a similar composition.

PACO or **PACOS**. A Peruvian term for a ferruginous earth or ore containing small quantities of metallic silver.

PÆONINE (*Red Coralline* or *Aurine R.*) *v.* AURINE.

PAINTS. *Definition.*—Coloured compositions, usually liquids, which can be applied with a brush to suitable surfaces. The coverings formed are either dull or only moderately lustrous; and they often act as protectives and preservatives of the surfaces beneath. Generically, paints differ from varnishes in yielding coatings possessing less lustre, and in the absence of resinous ingredients; but there are certain exceptions to this. Ordinary paints consist essentially of two parts, the *pigment* or colouring agent, and the *medium* or vehicle. A third constituent, the drier, is often present; and in some paints, manufactured for particular uses, such as luminous paints, anti-corrosive paints, and waterproof paints, other components of the most various descriptions are met with.

In this article the term 'pigment' will be confined to those substances to which paints owe their colours, while 'paint' will be employed in reference to the combination of pigment and medium, ready for use by the painter. Certain pigments will be first described, and then the vehicles by which these pigments are converted into paints. Driers will next be referred to; and, lastly, paints themselves.

Pigments. *Definition.*—Finely divided solids, insoluble in water, and yielding paints when intimately mixed with suitable media.

Origin.—Pigments are obtained from animal, vegetable, and mineral sources, chiefly the last. Inorganic pigments comprise minerals and manufactured products, mostly metallic salts or oxides; such pigments are usually more permanent than those of vegetable or animal origin.

Characters.—1. Body or covering power, *i.e.* the property of completely covering and concealing the surface beneath. 2. Drying property, when combined with a medium to form paint. 3. Durability. 4. Quality of tint.

Pigments may be of all degrees of opacity, and they also differ greatly from one another in density and in the state of aggregation of their particles. Some are opaque and amorphous; others are crystalline and translucent or transparent. The greater the density and opacity of a pigment, the greater is its body. Crystalline powders, however impalpable, have less opacity than amorphous powders, hence the great superiority as regards covering power of the latter. The drying property of a pigment (in an oil paint) depends upon its power of oxidising or promoting the oxidation of the medium with which it is mixed; this property is possessed in a much greater degree by some pigments than by others. And siccatives or driers must be added when the pigment is known to be deficient in this oxidising or drying power. Durability is tested by the power of the pigment, when made into paint, of resisting the action of moisture, fetid gases, acid vapours, exposure to the atmosphere, &c. As a rule, pigments are more durable when mixed with oil than when in the form of water-colour paints. Quality of tint depends largely upon the exact manner in which the manufacture of a pigment has been carried out. In a case, for example, where the pigment has been precipitated from a solution, the shade of colour will vary with the amount of care devoted to the washing of the precipitate —a very small percentage of impurity being the cause of a marked difference in the tint. The degree of subdivision of a pigment also has a most important influence on its colour.

Preparation.—The pigments of commerce are so exceedingly numerous that it will be impossible to describe the different manufacturing processes by which they are obtained (an exception will be made, however, in the case of white lead, for the reason given under that heading); but the important operation of grinding must be alluded to. It is absolutely essential that every pigment shall be in an extremely fine state of division. The colours made use of by house-painters and paper-stainers are pulverised and mixed by paint-grinders, while the more numerous and brilliant pigments used in the fine arts are ground by artists' colourmen. Formerly, most pigments were ground by hand on a grinding stone with the aid of a muller, but the unhealthy and dangerous nature of the operation, especially when orpiment, white and red leads, chrome yellow, and many other important pigments, were treated, led to the introduction of colour mills, in which larger quantities of pigments can be ground, and mixed in covered vessels, so that the risk to the workmen is very greatly lessened. [For construction and figures of colour mills, paint-mixers, &c., reference may be made to Audés, Bolley-Birnbaum's Handb. d. Chem. Technol., Neue Folge, Liefg. 4, 1882, 100–112; *v.* also Schlager, Germ. Pat. 18,952, Feb. 1882, and Clark, Eng. Pat. 16,034, Nov. 6, 1888.]

The best-known pigments, classified according to colour, will now be considered, and particulars will be given of their origin and composition. Many unimportant and little-used pigments will be intentionally omitted. For further details *v.* PIGMENTS.

WHITE PIGMENTS.

White Lead (*Céruse, Blanc de Plomb, Bleiweiss*). As this important pigment is the basis of almost all paints in ordinary use (excluding artists' colours), and, indeed, constitutes about nine-tenths of their composition—the other pigments present being technically called the 'stainers'—a fuller account of it is necessary than of the rest of the pigments. The history of paints may almost be said to be conterminous with the history of white lead.

Composition.—White lead is a hydroxycarbonate of lead, but its composition is undoubtedly variable, among the numerous formulæ given being the following:—(Rose)—$6PbCO_3.2PbH_2O_2$; or $5PbCO_3.2PbH_2O_2$; or $3PbCO_3.2PbH_2O_2$. (Mulder, 33, A. 242)—$5PbCO_3.3PbH_2O_2$; or $3PbCO_3.PbH_2O_2$; or $2PbCO_3.PbH_2O_2$. (Phillips, C. J. 4, 165)—$2PbCO_3.PbH_2O_2$, usually; or $3PbCO_3.PbH_2O_2$; and, of one sample, $5PbCO_3.PbH_2O_2$. (Grüneberg, Polyt. Centralbl. 36, 1404)—$2PbCO_3.PbH_2O_2$. (Bolley, Hdb. d. Techn. 11, Bd. 5, Liefrg. 1, 483, *et seq.*)—$3PbCO_3.PbH_2O_2$; or $2PbCO_3.PbH_2O_2$. (Wigner and Harland, A. 2, 208, and Muter, Pharm. Chem.)—$3PbCO_3.PbH_2O_2$ (Church, A. H.)—$2PbCO_3.PbH_2O_2$. (Atkinson, S. C. I. 5, 312)—Japanese white lead, $2PbCO_3.PbH_2O_2$; and (Carter Bell, S. C. I. 3, 627) $3PbCO_3.PbH_2O_2$; or $2PbCO_3.PbH_2O_2$. Good white lead is either $2PbCO_3.PbH_2O_2$ or $3PbCO_3.PH_2O_2$. The latter formula is equivalent to 12·30 p.c. of CO_2, and, according to Wigner and Harland, *op. cit.*, samples containing much more or much less CO_2 are of inferior quality. Grüneberg (*op. cit.*) states that white lead containing more PbH_2O_2 than is represented by the formula $2PbCO_3.PbH_2O_2$ will turn yellow in a few hours when mixed with oil and kept from the light, a paint made from pure PbH_2O_2 turning yellow in the dark in forty-eight hours. White lead of the formula $3PbCO_3.PbH_2O_2$ is most generally approved, and the PbH_2O_2 should neither exceed nor be much below 25 p.c. (Carter Bell, *op. cit.*).

Characters of good white lead.—A perfectly amorphous white pigment, possessing great opacity, density, and covering power, and the property of drying rapidly, when mixed with linseed or a similar oil, and exposed to the air. The hydroxide combines with the oil, forming a white elastic coating or paint; but lead hydroxide alone would give little opacity, which is imparted by the carbonate present. The latter forms an emulsion with the oil, of extreme opacity. Both, then, are essential.

Manufacture.—The oldest, and so-called Dutch or 'stack,' process is still carried on to a large extent in Holland, Belgium, parts of Germany, and in this country. Metallic lead is exposed to the action of acetic acid vapour, moisture, air, and carbonic acid, in the following manner. Coils, buckles, or gratings of lead are supported on wooden frames in earthenware pots, 4 or 5 inches in diameter and 7 or 8 inches high, containing a little acetic acid or vinegar and covered with leaden plates. The pots are imbedded in layers of fermenting horse-dung, or tanners' refuse, or a mixture of the two, and above are laid wooden planks, on which are other pots, similarly charged and imbedded in dung, or tan, or both. A succession of such layers constitutes a stack, and the operation is often conducted in large brick chambers, capable of holding 70 tons of stacked lead. Carbonic acid and water vapour are produced by the decomposition of the organic matter; the temperature of the stack gradually rises to 38–65°C.; and a mixture of acetic acid vapour, carbonic acid and moist air rises and passes over the surface of the lead. Lead oxide is at first formed, and is converted into basic acetate by the action of the acetic acid and water vapour. A portion of the lead oxide present in the basic acetate is converted into white lead by the action of the carbon dioxide, normal lead acetate being at the same time produced. The normal acetate is reconverted into sub-acetate by taking up fresh lead oxide, and is then in a condition to be again attacked. This action is allowed to proceed until the temperature of the stack begins to fall, generally in 3 to 4 months' time. The stack is now stripped, and the coils or gratings of lead, coated with white lead, which should consist of regularly deposited layers of a compact, porcellaneous character, are removed, moistened with water, and passed between rollers. The detached crust is next ground with water under heavy edge runners, and afterwards passed through horizontal mills into settling tanks. The final operations are drying and packing. The deposited white lead is sometimes transferred to skips and agitated by a 'dolly,' before conveyance to the drying chamber (Carter Bell). A German modification of this process consists in exposing strips of lead on laths placed lengthwise in chambers, the floors of which are covered with spent tan, marc of grapes, &c., saturated with vinegar. Sometimes steam is admitted through perforations in the floor or false bottom of the chamber. Another method adopted in Germany is to place granulated lead, moistened with vinegar, on hurdles in wooden boxes, carbon dioxide being supplied, and the temperature being raised by steam to 35°C. Time, eight to ten weeks. In Great Britain, a process much followed is treatment of litharge with water and 1 p.c. by weight of normal acetate, or nitrate of lead (Watts' Dictionary of Chem. first ed. 1, 786). The mass is placed in a series of closed troughs, communicating with each other, and CO_2 is admitted. The Japanese method of manufacture is founded on the same principle as the Dutch process—namely, exposure of metallic lead to acetic acid, air, moisture, and CO_2; the product has the percentage composition, PbO, 86·42, CO_2, 11·60, and OH_2, 2·00 (R. W. Atkinson, S. C. I. 5, 312). Nearly all the white lead of the world is made by one or other of the direct methods already described, although attempts to introduce other processes have been exceedingly numerous. Among *earlier* patents may be mentioned those of Leigh—precipitating chloride of lead solution by ammonium carbonate: Pattinson (Sept. 1841)—precipitating a solution of lead chloride by magnesium bicarbonate solution, and triturating the lead carbonate produced with caustic potash or soda solution, in order to convert any unchanged $PbCl_2$ into PbH_2O_2: Spence—obtaining white lead directly from lead ores: Button and Dyer—preparing basic lead acetate from litharge, and subjecting to the action of carbon dioxide: Paller (1859)—moistening lead, previously finely divided by the aid of a centrifugal machine, with acetic acid, treating the resulting acetate and carbonate with acetic acid, and depositing the white lead in a settling tank: Grüneberg (1860)—submitting granulated lead while in rapid motion to the simultaneous action of air, acetic acid, and carbon dioxide: Tourmentin—mixing basic lead chloride, obtained by the action of sodium chloride on litharge, with water, passing in CO_2, and boiling the fluid in leaden pans with chalk; the deposited white lead being freed from salt by washing with water; and Krafft—manufacture from sulphate of lead, by boiling with barium acetate; white lead and barium sulphate (also used as a pigment) being produced together. Another method suggested was to digest sulphate of lead with sodium or ammonium carbonate.

In some of these methods, the metal was granulated; the especial feature of others was the particular kind of apparatus employed; in several, a salt of lead, such as $PbSO_4$ and $PbCl_2$, or the oxide, litharge, was substituted for metallic lead; and in at least the majority of cases the pigment was *precipitated.* Precipitation-processes, in particular, seem to attract inventors; but they possess the disadvantage of yielding, not an amorphous, but a crystalline product. However finely ground the pigment, its particles are always transparent and of a crystalline character, so that the paint yielded by it must be deficient in body or covering power; and it is doubtful whether the crystalline particles can so readily combine with the oil.

One of the most familiar of the precipitation-methods is that known as the French process, invented by Thénard & Roard, and carried on now at Clichy, near Paris. Litharge is dissolved in acetic acid, and carbon dioxide is passed into the solution of basic acetate produced. Many other precipitation methods have been proposed: the following are outlines of some of the more recently invented processes:—Milner (Eng. Pat. 4,053, Nov. 22, 1875; an improvement on previous patents, Dale & Milner, Eng. Pat. 2,442, Aug. 10, 1869, & Milner, Eng. Pat. 1,881, June 22, 1872)—preparation of insoluble basic chloride of lead, by agitating litharge, salt, and water together, and suspension of the basic lead chloride in a mixture of caustic soda and sodium chloride solutions; finally treatment with CO_2 in a lead-lined vessel: Schnabel (D. P. J. 246, 300) dissolves PbO, obtained as a residual product in the manufacture of zinc white, ZnO, in warm acetic acid, and precipitates the resulting basic lead acetate solution with CO_2: Condy (Eng. Pat. 1,095, Mar. 14, 1881; Eng. Pat. 1,693, Jan. 18, 1884) granulates lead, places it in tanks where it is alternately exposed to air and dilute acetic acid, at short intervals, and precipitates the basic acetate solution obtained with sodium bicarbonate; the whole operation is said to be effected in seven days. According to a later patent (18,705, Dec. 21, 1888), Condy uses carbon dioxide, followed by an alkaline carbonate. Blyth (Eng. Pat. 10,375, July 19, 1884) treats litharge with a solution of normal acetate of lead in a vessel with a false bottom, and precipitates with CO_2 supplied from beneath: Roth & Sylvester (D. P. J. 252, 372; Amer. Pat. 292,119, Jan. 15, 1884) employ electricity; the current is passed through a solution of sodium acetate, leaden plates being used as the electrodes; lead acetate and caustic soda are formed, and produce PbH_2O_2 by mutual reaction; this is converted into white lead by a stream of CO_2: Wilson (Eng. Pat. 6,464, Ap. 17, 1884) obtains basic acetate of lead by the alternate action of air and steam, and of normal lead acetate or nitrate, upon finely divided metallic lead, contained in a revolving drum provided with shelves; the precipitation is effected in another vessel: Anderson (Eng. Pat. 5,166, Dec. 18, 1884) submits lead in a rotating drum, to the alternate action of a hot blast of air and the solvent liquid, precipitation being accomplished either in the drum itself or in a separate vessel: Eyckens (Eng. Pat. 1,832, Feb. 8, 1886) makes use of the facts that a solution of lead nitrate converts lead into lead hydroxide, itself becoming lead nitrite, and that lead nitrite, on the prolonged action of lead, parts with another molecule of oxygen, forming lead hydroxide and nitric oxide. The latter is reoxidised by atmospheric oxygen into a mixture of nitrous and nitric acids. These, together with PbH_2O_2, produce lead nitrite and nitrate, the solution of which can again oxidise and dissolve lead. Polybasic salts are formed by the combination of the lead hydroxide and lead nitrite, and Eyckens finds that carbon dioxide can return such polybasic salts to the normal condition by precipitating the excess of base as $PbCO_3 + PbH_2O_2$, thus: $[Pb(NO_2)_2.3PbO] + 2H_2O + 2CO_2 = Pb(NO_2)_2 + H_2O + 2PbCO_3.PbH_2O_2$. A relatively small quantity of lead nitrate, which is constantly being regenerated, can convert an indefinitely large quantity of lead into white lead. In working the process, shavings of lead are put into a closed cylindrical chamber or converter, together with a solution of lead nitrite, and a mixture of air and carbon dioxide, suitably heated, is injected. The gases pass from the converter through towers filled with polybasic lead nitrite. This retains all free nitrous acid, and is converted into normal $Pb(NO_2)_2$. The liquids are frequently transferred between the converter and towers, and the white lead collects at the bottom of the converter, whence it is drawn off as fast as produced, for filter-pressing, washing, and drying: Löwe (Eng. Pat. 9,122, June 27, 1887) precipitates lead carbonate from a solution of lead nitrate or acetate, by adding sodium or potassium bicarbonate, and he adds to the carbonate so produced basic lead acetate, white lead being deposited: Orr (Eng. Pat. 15,406, Nov. 11, 1887) adds to litharge, mixed with water under slight pressure, acetic, propionic, valerianic, butyric, or nitric acid, and subsequently injects into the mixture carbonic acid: MacIvor and others (Eng. Pat. 10,426, July 18, 1888, and 6815, Ap. 23, 1889) cause ammonium acetate to act upon lead oxide, carbon dioxide being afterwards introduced. The white lead formed can be filtered off, and the solution of ammonium acetate is used in the conversion of a fresh charge of lead oxide: Bronner (Eng. Pat. 16,706, Oct. 22, 1889) prepares basic lead sulphate by heating $PbSO_4$ with soda-lye, and converts the $2PbSO_4.PbH_2O_2$ into white lead by heating with sodium carbonate, according to the equations:

(*a*) $3PbSO_4 + 2NaOH = 2PbSO_4.PbH_2O_2 + Na_2SO_4$,
and (*b*) $2PbSO_4.PbH_2O_2 + 2Na_2CO_3 = 2PbCO_3.PbH_2O_2 + 2Na_2SO_4$.

A very satisfactory product is stated to be yielded by this method, the cost of which is said to compare favourably with that of the stack process: Zeitler's method (Eng. Pat. 2,812, Feb. 16, 1891) is not dissimilar: finally, there is the method of Tibbits (agent, Lake, Eng. Pat. 18,076, Nov. 12, 1889), according to which a lead electrode is electrically dissolved in an electrolyte containing free or nascent carbon dioxide, the lead compound formed by electrolytic action being precipitated to form white lead.

Many modifications of the direct method of manufacture have also been suggested, some of them with the view of substituting, for treatment in open chambers to which workmen must have access, operations in closed vessels or chambers, from which the exceedingly injurious vapours and dust generated in the older processes cannot escape. The chief patents which have been taken out of late years are here enumerated. Thompson (Eng. Pat. 4,056, Oct. 6, 1880, and 18,431, 1881) conveys perforated sheet lead on trucks into a chamber heated by steam pipes, provided at the bottom with troughs charged with dilute acetic acid, and supplied with air and CO_2 by glass pipes. The invention of Morris (Eng. Pat. 13,444, Sept. 18, 1888) is in some respects similar. Gardner (Eng. Pat. 731, 1882; Germ. Pat. cl. 22, 25,239, Aug. 19, 1882) granulates lead by dropping it into a tank of lead acetate or nitrate solution, and transfers to chambers heated to 37·7°C., and so constructed that the lead, its supports, and the lining of the chamber connected with these supports, constitute a battery of galvanic pairs or couples. Acetic acid vapour, ozonised air, moisture, and CO_2 are supplied to the chamber during the earlier part of the process; then steam and air, at 49–54°C.; and, lastly, air only. The dried contents of the chamber are next transferred to a revolving iron cage, in which the white lead is separated from the blue lead, ready for treatment by crushing rollers, mixers, paint-mills, &c. This process is said to answer satisfactorily, and to occupy only about fourteen days. Kirberg (D. P. J. 253, 296; Ger. Pat. 27,398, Nov. 28, 1883) places the lead to be converted on carriers, so suspended in entirely closed and dust-tight chambers that the material can be agitated from without, ready-formed white lead being thus shaken off, and a fresh surface of the metal exposed. Hand Smith (Eng. Pat. 5,862, Dec. 26, 1883) employs a corroding chamber inclosed in an outer vessel heated to 49–60°C. Air and CO_2 are supplied to the interior of the chamber, under a slight pressure, and through diaphragms of a textile fabric saturated with dilute acetic or nitric acid; or a tray of concentrated acid may be put on the floor of the chamber. Haylor, Read, & Percival (Eng. Pat. 13,115, Oct. 30, 1885) use chambers, the floors of which are covered with acetic acid and heated by steam-pipes. Perforated boxes, with their edges immersed in the acid, supply air and CO_2 from without. The incrusted leaden gratings are removed by lifts, travelling bands, or otherwise to the mill. Warwick (Eng. Pat. 5,820, Ap. 29, 1886) converts lead, previously granulated, into white lead, in a circular chamber, provided with shelves so arranged that the metal passes very gradually from top to bottom, meeting, during its descent, rising water- and acetic-acid vapours, mingled with air and CO_2. The white lead produced is broken up by granite balls, in a horizontal revolving drum, into which air is blown at the same time; the finer particles of the pigment are thus ejected into a dust-chamber, from which they are afterwards removed, for use as an especially fine and pure preparation. The powder remaining behind is thrown into water and ground under edge runners. [For other novelties or improvements, more especially connected with apparatus and plant, see the following:—Martin, Eng. Pat. 1,054, Mar. 18, 1879; D. P. J. 254, 489; Ger. Pat. 28,322, Aug. 31, 1883: Kay, Eng. Pat. 727, Jan. 5, 1884: Kirberg, D. P. J. 254, 489; Ger. Pat. 28,528, Jan. 9, 1884: Bennett, Eng. Pat. 8,725, July 3, 1886: see also, for other information relative to White Lead Manufacture:—v. Weise, D. P. J. 208, 434; C. J. 26, 1268: Wittstein, D. P. J. 212, 223; J. 1874, 1119: Hampe, Am. Ch. 5, 241; J. 1875, 1074: and Zeitler, Eng. Pat. 2,812, Feb. 16, 1891.] *V. White lead*, art. Lead.

Adulterations of white lead.—Barium sulphate and chalk principally; but calcium sulphate, clay, lead sulphate, &c., are also added. Most of the cheaper so-called white lead in the market contains an admixture of barium sulphate or some other adulterant. Some of these substances are themselves used as white pigments of inferior quality.

Substitutes for white lead.—The chief, if not the only, objections to white lead as a pigment are its poisonous character and its tendency to darken in an atmosphere containing sulphuretted hydrogen. Many substances have been proposed as substitutes, but all are inferior to white lead in body. Sulphate of lead (Richardson, 1834); oxychloride of lead, Pb(OH)Cl (Pattinson, 1849), prepared by precipitating a hot solution of lead chloride with lime water; zinc oxide; zinc sulphide; and a mixture of oxide, sulphide, and sulphate of zinc, have been manufactured for this purpose. Most of these compounds are less injurious to health than white lead, but it is hardly necessary to state that only the zinc compounds retain their colour when exposed to sulphuretted hydrogen. Griffiths' 'Patent Zinc White,' $5ZnS + ZnO$, is said by Phipson (C. N. 38, 105; C. J. 34, 1017) to possess considerable covering power. It is prepared by precipitating zinc chloride or sulphate with a soluble sulphide, calcining the precipitate, and plunging it while hot into cold water. Freeman's 'Patent Non-Poisonous White Lead' is especially prepared lead sulphate, together with 25 p.c. of zinc oxide, and is said to be but slightly affected by sulphuretted hydrogen. A mixture of zinc sulphide with barium and strontium sulphates constitutes the pigment-base in Orr's 'Charlton White' and 'Duresco.' Other white-lead substitutes have been invented—*v.* French, Eng. Pat. 5,193, Nov. 1883, an oxychloride of lead, prepared in the working of a previous patent (2,494, June 18, 1881): Ward, Eng. Pat. 10,838, Sept. 12, 1885: Lyte, Eng. Pat. 10,298, Aug. 11, 1886, 11,889, Sept. 18, 1886, and 2,920, Feb. 27, 1888—basic carbonate, chloride, phosphate, and sulphate of lead: Hannay, Eng. Pat. 13,416, Oct. 21, 1886, 1,282, Jan. 24, 1889, and 1,434, 1889—lead sulphate: Freeman, Eng. Pat. 4,879, Oct. 13, 1882; and 13,891, Nov. 13, 1885; Spence, Eng. Pat. 14,128, Nov. 18, 1885—zinc sulphide and barium sulphate or carbonate: Kenyon, Eng. Pat. 4,334, Mar. 23, 1887—zinc sulphide and barium sulphate: Fell (agent, Johnson), Eng. Pat. 722, Jan. 15, 1889—basic lead sulphite: and Wood, Eng. Pat. 19,910, Dec. 11, 1889—lead and zinc sulphates and carbonates.

For other white pigments and methods of preparation, *v.* Schmidtmann, Ger. Pat. 21,987, April 1882—zinc oxide: Griffiths, Eng. Pat. 750, 1883 (ZnS, &c.): Knight, Eng. Pat. 795, 1882—zinc: Rickmann, Ger. Pat. 19,073, Jan. 1882—barium sulphate: Claus, Eng. Pat. 4,107, Aug. 28, 1882—zinc sulphide: v. Gelder, Ger. Pat. 21,911, Aug. 1882—oxide and silicate of zinc: Bunn, Eng. Pat. 8,008, July 1, 1885—lead pigments: Hannay and Pape, Eng. Pat. 9,581, July 24, 1886—mixture of zinc oxide with sulphide or chlorosulphite of lead: Gunn, Eng. Pat. 955, June 21, 1887—zinc sulphide and barium sulphate: Martin, Eng. Pat. 6,619, May 5, 1887—mixtures of barium sulphate and calcium sulphate with zinc oxide, &c.: Schnabel, D. P. J. 246, 300: and Grimshaw, Eng. Pat. 985, Jan. 20, 1890—basic chloride of zinc.

It now only remains to refer to the names by which the various white pigments met with in commerce are known, and to a few white pigments which have not yet been mentioned. *Flake white* and *Krems white* are names applied to very fine and pure varieties of white lead. *Venice*, *Hamburg* and *Dutch whites* are mixtures of white lead and barium sulphate in different proportions. *Blanc fixe*, *Baryta white*, and *Permanent white* are barium sulphate. *Strontium* or *Strontian white* is sulphate of strontium. Magnesia (MgO) and magnesium carbonate ($MgCO_3$) constitute *Magnesia whites*. *Spanish white* is whiting, $CaCO_3$. *Zinc white* and *Chinese white* are names given to zinc oxide. (The term *Chinese white* has, however, sometimes been applied to barium sulphate.) Carbonate of zinc has also been employed as a pigment, but not very successfully. *Pearl white* is basic nitrate of bismuth, $Bi(OH)_2NO_3$; but the name is also used in connection with a lead white, tinted with indigo or some other blue pigment. Yet another *Pearl white* is $6BiOCl.Aq$; and basic nitrate of bismuth is occasionally called *Flake white*. Whites of tin, cadmium, mercury, arsenic, tungsten, and antimony have all been used, but without permanent success. Antimony white, however, is said to have considerable covering power. The zinc and baryta whites are frequently used, but, though unaffected by sulphuretted hydrogen, they are deficient in body. Indeed, good white lead has in this latter respect a pre-eminence over all other white pigments hitherto discovered. Moreover, it has much better drying qualities.

YELLOW PIGMENTS.

Yellow ochre, *Terra di Sienna*, *Stone yellow*, *Roman yellow*, *Mineral yellow*, *Oxford ochre*, *Golden ochre*, &c. Argillaceous earths, containing varying percentages of hydrated ferric oxide (very durable and trustworthy pigments). *Mars yellow*, an artificial preparation of similar composition. *Chrome yellow*, $PbCrO_4$: also $PbCrO_4.PbSO_4$; and $PbCrO_4.2PbSO_4$. *Cologne yellow*, $PbCrO_4$, $PbSO_4$, and $CaSO_4$. (These yellows possess considerable body, but are affected by sulphuretted hydrogen.) *Strontium*, *Barium*, and *Zinc yellows*, $SrCrO_4$, $BaCrO_4$, and $ZnCrO_4$ (durable, but have little body). Barium chromate (*Lemon yellow*, *Yellow ultramarine*) is the most permanent of these pigments. *Bismuth yellow*, also a chromate (not permanent). *Cadmium yellow*, CdS, durable, and of fairly good body. True *Naples yellow*, PbO,Sb_2O_5 (permanent in oil). Cadmium sulphide, and a pale yellow ochre, have been sold under the same name. *Montpellier*, *Cassel*, *Turner's*, *Turin*, *Verona*, and *Paris yellows*, oxychlorides of lead (not lasting). *King's yellow* or *Orpiment* (unstable). *Wolfram*, *Vanadium*, *Uranium*, *Thallium*, *Palladium*, *Tin*, *Antimony*, and *Platinum yellows* (most unstable and little used). *Indian yellow* or *Purree*, impure magnesium euxanthate, $C_{19}H_{16}MgO_{11},5H_2O$, prepared from the urine of cows fed on mango-leaves (Church). A beautiful but variable pigment. *Madder yellow*, *Italian pink*, *Brown pink*, &c. (vegetable: non-durable—bleached on exposure). *Gamboge* (a vegetable resin; unstable). *Aureolin*, nitrite of cobalt and potassium, $K_6Co_2(NO_2)_{12},3H_2O$ (fairly permanent). [For other yellow pigments and preparation of, *v.* Werner, Eng. Pat. 5,291, 1881—chrome yellow: Weber, S. C. I. 4, 671, and D. P. J. 279—chrome yellows, mixture of, with kaolin, barium sulphate, calcium sulphate, &c.: Massignon and Watel (agent, Lake), Eng. Pat. 2,224, Feb. 6, 1891—chromium compounds: Swan, Eng. Pat. 2,360, Feb. 17, 1886—an iron-yellow: and Buchner, Chem. Zeit. 11, 1087–1089; 1107–1109; and Chem. Trade Journ., May 30, 1891—cadmium yellows.]

RED PIGMENTS.

Vermilion, *Cinnabar*, H_3S (moderately permanent in oil: alterable in water-colour). *Minium*, *Red lead*, Pb_3O_4 (not permanent). *Light red*, calcined yellow ochre; *Indian red*, *Venetian red*, *Rouge*, *Colcothar*, *Bole*, *Caput mortuum*, &c.: ochres (all durable colours). Some of these pigments are artificially obtained by calcining ferrous sulphate. *Chrome red* or *Austrian cinnabar*, basic lead chromate, $PbCrO_4.PbH_2O_2$, and *Chrome oranges*, mixtures of normal and basic lead chromates (all unstable). *Realgar*, arsenic sulphide. *Antimony vermilion*, antimony sulphide. *Palladium red*, ammonio-chloride of palladium, and mercuric iodide (very unstable), have been used. *Madder* lakes (vegetable colours on mineral bases; unreliable). *Carmine lake* (of animal origin—from *Coccus cacti*; a beautiful colour, but not permanent). [*V.* also Werner, Eng. Pat. 5,291, 1881—chrome-red. Martin, Eng. Pat. 5,192, Mar. 20, 1884—vermilion from lead oxide, said to equal genuine vermilion in durability; also '*vermilionettes*,' combinations of white lead or white zinc with eosine; very fugitive: Swan, Eng. Pat. 2,310, Feb. 17, 1886—a red pigment, by treatment of ferrous chloride: Jones, Eng. Pat. 7,761, May 27, 1887—iron oxides: Buchner, Chem. Zeit. 11, 1087–1089; 1107–1109—a vermilion, consisting of a polysulphide of cadmium: Mercier, Ann. Ch. Pharm. 160, 252—red lead: and Larrouy, Eng. Pat. 3,786, Mar. 10, 1890—red lead.]

GREEN PIGMENTS.

Terre verte, an impure ferrous silicate (permanent, but destroyed by acids). Copper greens —*Malachite*, *Mountain green*, or *Green verditer*, hydroxycarbonate of copper, $CuCO_3,CuH_2O_2$, *Scheele's* (arsenite), *Schweinfurt* or *Emerald green* (acetoarsenite), *Brunswick* (oxychloride), and *Elsner green* (stannate) are among the best known. The phosphate, bisulphate, borate, chromate, and sub-acetate (*verdigris*) have also been employed as pigments. *Nitis*, *Vienna*, and *Kirchberger greens* have the same composition as Scheele's green. *Bremen*, *Green ashes*, *Paul Veronese green*, and *Mineral green*, are other copper pigments. All are darkened by sulphuretted hydrogen, and most are very poisonous.

Mixed greens.—Brunswick green (another kind), German green, Hooker's, Leaf-, Milory-, and Silk-greens are mixtures of yellow and blue pigments, chiefly chrome-yellow and Prussian or other blues.

Chromium, *Guignet's*, *Pannetier*, *Arnaudon*, *Matthieu-Plessy*, and *Chrome emerald greens* are hydrated sesquioxides of chromium, with phosphate or borate of chromium. *Viridian* is $Cr_2O_3,2H_2O$. All are permanent and full-bodied pigments (*v.* CHROMIUM). *Rinmann's green*, *Cobalt green*, or *Zinc green*, a compound of oxide of cobalt and oxide of zinc. *Titanium*, *Vanadium*, *Uranium*, *Manganese*, *and Molybdenum greens* are also occasionally met with as pigments. *Green ultramarine* is produced in the manufacture of artificial ultramarine. There are many unstable green lakes of vegetable origin, such as *Chinese green*, *Iris green*, and *Sap green*, but they are of little or no value. [*V.* Carnot, C. R., July 18, 1881—recommendation of chromium phosphate as a fine green pigment; Pichot and Grangier, S. C. I. 7, 573—manufacture of green and other varieties of ultramarine; Donath, D. P. J. 263, 246–248—a manganese green, barium manganate; Blount, A. 13, 66—'Navy-green paint,' the pigments in which were barium sulphate, lead chromate, and an organic blue of doubtful nature; and Douglas, C. N. 40, 59; C. J. 36, 987.]

BLUE PIGMENTS.

Prussian blue, *Berlin blue*, &c., $Fe_7(CN)_{18}$ (liable to change). *Soluble Prussian blue*, of inferior quality to the preceding, is $K_2Fe(CN)_{12}Fe_2$. *Indigo* $C_{16}H_{10}N_2O_2$ (vegetable; fades on exposure). *Native ultramarine*, pulverised lapis lazuli (an excellent and stable, but costly colour). *Artificial ultramarine*, a compound of silicate of aluminium and sodium, with sulphide of sodium; suggested by Gmelin, in 1827, and made by Guimet in 1828. Less expensive than native ultramarine, and nearly equal to it as a pigment. Both pigments are permanent in the absence of acids (*v.* ULTRAMARINE). *V.* Pichot and Grangier, *op. cit.*; and Bouillet, Eng. Pat. 9,176, July 14, 1886, for manufacture of ultramarine, &c. *Thénard's blue*, phosphate and aluminate of cobalt. *Cobalt blue*, *Gahn's ultramarine*, aluminate of cobalt. *Cyanine*, *Leitch's blue*, a mixture of cobalt blue and Prussian blue. *Smalt*, *Zaffre*, *Royal*, and *Saxony blues*, glasses coloured by cobalt oxide. *Cœruleum*, $3(SnO_2.CoO) + SnO_2$ (stannate of cobalt). The cobalt colours lack somewhat in body and permanency. *Copper blues*, carbonates, silicates, and other salts of copper, are of little value. *Molybdenum blue*, $4MoO_3 + MoO_2$, a product of the reduction of molybdic acid. F. Fouqué (C. R. 108, 325–327) has described 'Egyptian blue,' a colouring matter, $CaO,CuO,4SiO_2$, which was used by the Romans during the first few centuries of the Christian era. Fouqué has prepared this pigment by a method given by Vitruvius, and writes in the highest terms of its stability and beauty (*v.* EGYPTIAN BLUE).

BROWN PIGMENTS.

Vandyck, *Rubens*, *Cassel*, *Ulmin*, and *Cologne browns*: these are partly of vegetable origin, and are prepared from peat, cotton, soot, &c.; bituminous matter is often present. *Burnt sienna*, *Brown terre verte*, *Raw* and *burnt umber*, *Cappagh brown*, and *Mars brown*, are earths or ochres, raw or calcined. Most of them are durable and reliable pigments. Other browns are *Prussian brown*, made by calcining Prussian blue; *Madder brown* (of vegetable origin, and liable to fade); *Bistre*, a bituminous brown; *Asphaltum*; and *Mummy*. The last three are also untrustworthy pigments.

BLACK PIGMENTS.

Ivory black, *Bone black*, *Lamp black*. These are more or less pure carbon, and the names are self-explanatory. *Indian ink* consists of very fine lamp black, together with gelatin and a perfume (*v.* INDIAN INK). *Blue-black* is made by carbonising vine-twigs, and the like. *Manganese black* is native peroxide of manganese. All these black pigments are very durable. *Sepia* is a brownish-black pigment derived from the ink-bag of *Sepia officinalis*: it is alterable by sunlight, but less so than *Vandyck brown*, &c.

Of the above-mentioned pigments only a few (chiefly the ochres, lamp-black, red lead, white lead, zinc white, baryta white, Prussian blue, chrome yellow, orange and red, vermilion, and the commoner copper greens) enter into the constitution of the paints used by decorators and house-painters; white lead is nearly always the base, and is largely in excess of the other pigments present, which are technically called the '*stainers*.' The finer varieties of these colours and many of the other pigments, are used either habitually or occasionally by artists. Of pigments not named in this article, there are many which are simply fancy preparations, with no good qualities to recommend them.

As regards durability, it may be shortly stated that all the compounds of copper, lead, and bismuth, and some mercurial pigments, darken more or less, when exposed to air containing sulphuretted hydrogen. Most of the colours which are partly or entirely of organic origin fade on exposure, by a process of oxidation. On the other hand, pigments which are not affected by foul gases, the barium and zinc whites, for example, have unfortunately, for the most part, less covering power than the majority of lead, copper, and other changeable pigments. Great circumspection must, therefore, be exercised in the choice of a pigment, whether for artistic or ordinary work. As a rule, pigments are less fugitive in oil-media than when mixed with the usual water-colour vehicles. Church (The Chemistry of Paints and Painting, 1890, 226) classifies artists' pigments as follows, according to their stability in oils:—

Class I. Truly permanent.	Class II. Somewhat changeable.	Class III. Untrustworthy.
Baryta white.	Aureolin.	King's yellow.
Zinc ,,	Baryta yellow.	Yellow madder.
× Flake ,,	Indian ,,	Brown pink; yellow lake.
Yellow ochre.	Strontia ,,	Gamboge.
Raw sienna.	× Chrome ,,	Zinc chromate.
× Naples yellow, true.	Madder carmine.	Crimson lake.
× Cadmium ,,	Rubens madder.	Carmine and burnt carmine.
Cadmium orange.	Rose ,,	Indian lake.
× Vermilion, artificial.	Madder red.	Scarlet ,,
Vermilion, native.	Purple madder.	Purple ,,
Indian red.	Cobalt green.	Verdigris.
Light ,,	Emerald green (Schweinfurt g.)	Sap green.
Venetian red.	Terre verte.	Green vermilion etc.
Red ochre.	× Malachite.	Indigo.
Viridian (Emerald oxide of chromium $Cr_2O_3.2H_2O$).	Smalt.	Blue verditer.
Green oxide of chromium, Cr_2O_3.	Prussian blue.	Blue ochre.
Ultramarine.	Antwerp ,,	Bituminous Vandyck brown.
Artificial ultramarine.	× Madder brown and black.	
Cobalt.	Cologne earth.	
Cœruleum.	Bitumen.	
Burnt sienna.	Earthy Vandyck brown.	
Raw and burnt umber.		
Cappagh brown.		
Caledonian ,,		
Verona ,,		
Prussian ,,		
Ivory black.		
Charcoal black.		
Lamp-black.		
Graphite.		

To adapt the table to water colours, the pigments marked × must be relegated to class III.: while Indian ink, bistre, and sepia may be added to the table. The two latter must be placed in class III. however.

The following examples of carefully chosen palettes are quoted from Church's work, just cited (pp. 234-236): (*a*) for *oil-painting*, flake white, yellow ochre, cadmium yellow, aureolin, vermilion, madder carmine, ultramarine, viridian, Cappagh brown, and ivory black: (*b*) for *water-colours*, Chinese white, yellow ochre, cadmium yellow, aureolin, cinnabar, madder carmine, ultramarine, viridian, Mars brown, and Indian ink. A report of considerable importance was some time since submitted to the Government, setting forth the disastrous effects of sunlight and atmospheric oxidation upon water-colour drawings; and, undoubtedly, too much use has been made in this form of art of ill-chosen, unreliable, and, in many cases worthless colours (Russell and Abney, Action of Light on Water

Colours (Blue-book), London, 1888; also Hartley, Fading of Water-Colours, Brit. Ass. Rep., 1886, 584).

No account of the coal-tar colours is given here, as but few of them are pigments in the true sense of the word, and they are little used in painting.

[Additional information on the subject of pigments will be found in Bolley's Hdbk. d. Technol. 11, Bd. 5, Liefrg. 1, 483-520; Watts' Dict. Chem., 1st and 2nd ed., under the various headings; and Muspratt's Dict. Chem. last ed.; see also Ure's Dict. 1875, i. 894; Wigg, Steel, and Wigg, Eng. Pat. 11,129, Sept. 1885—pigments from chlorine and copper residuals; Huntington and Chiapponi, Eng. Pat. 12,723, Oct. 23, 1885—antimonial pigment. Grimshaw, Eng. Pat. 985, Jan. 20, 1890—white pigment, consisting of basic chloride of zinc; and Larrony, Eng. Pat. 3,786, March 10, 1890—production of red lead and litharge.]

Media or Vehicles. *Definition.*—The fluids with which pigments are intimately mixed by grinding, for the production of paints. For oil-paints, the vegetable drying or siccative oils are employed, and for water-colour paints, size, honey, and aqueous solutions of gums, &c., are in use. Oil of turpentine is frequently added to the oil medium, and acts partly as a 'thinning' agent and partly by somewhat accelerating the drying of the paint. Benzene has been similarly used. In tempera-painting, albuminous or gelatinous media are employed, and water-glass is the vehicle in stereochromy. Lime-water or baryta-water is used in fresco-painting. Other paint-media are also occasionally made use of, and will be presently referred to.

Oils. These are chosen for their drying properties, or, in other words, their power of absorbing oxygen when spread in thin layers and exposed to the atmosphere; by this oxidation a film of a drying oil gradually becomes converted into a coherent coating of a hard, elastic, varnish-like substance.

Linseed oil is the most important and most commonly used drying oil; it is met with in commerce under the names of *raw*, *refined*, *artists'*, and *boiled* oil. Raw oil is as expressed from the seeds. By agitation in lead-lined tanks with 1 p.c. of strong sulphuric acid, boiling with water or treatment with steam, and drawing off in settling-tanks from water and sediment, raw oil is converted into refined oil. Artists' linseed oil has been allowed to stand for weeks or months, then treated with litharge, and finally bleached by exposure. Other processes of refining are also used. Boiled oil has been heated in air to 130°C., or thereabouts, and maintained at that temperature for a little while. Raw linseed oil possesses great drying powers, which are considerably enhanced by the operation of boiling. Boiled oil is, therefore, a most important article to the painter. The drying power of boiled oil is still greater if litharge or some other drier has been added during the operation of boiling. The drier appears to act as a carrier of oxygen to the oil, and a definite chemical compound of the metallic oxide with linoleic acid is at the same time formed. Both raw and boiled linseed oil are used in the manufacture of ordinary paints, while for the more delicate colours employed in the fine arts, refined, and artists' oil are preferred.

Poppy, walnut, hempseed, grape-seed, and castor oils are also used in the manufacture of paints, particularly poppy, walnut, and hemp oils. These oils are, however, almost exclusively used by artists; and linseed oil holds its own as the most generally useful and applicable drying oil. It is often adulterated, among the additions being mineral and resin oils, Niger-seed oil, cottonseed oil, and menhaden (a fish) oil. Many substitutes have been suggested for linseed oil; among them the following may be noted: (1) A mixture of cottonseed oil, previously boiled with litharge, Burgundy pitch, Dutch oil, petroleum, essence of mirbane and valerian oil (Oster, Germ. Pat. 18,767, Aug. 1881). (2) A substitute for the linseed oil used in 'primings,' or first coatings, made by treating blood with lime-water &c. (Koll, Germ. Pat. 18,307, Sept. 1881). (3) A mixture of naphtha, resin, turpentine, and linseed oil (Manning, Am. Pat. 269,591, 1882. (4) Blood serum treated with a soluble silicate (Johnstone, Eng. Pat. 82, 1883). (5) A compound of blood, linseed oil, potassium chromate, petroleum, hydrochloric acid, resin, and water (Fischer, Eng. Pat. 2,539, Feb. 1, 1884). (6) Rectified resin oil, colophony, and a suitable drier (Williams, Eng. Pat. 577, Jan. 3, 1884). (7) Oil extracted from Indian corn, together with a drier (Banker, Eng. Pat. 12,031, Sept. 6, 1887). And (8) Euphorbia juice, with a solution of shellac (Hooper, Eng. Pat. 39, Jan. 1, 1885). Wirth (Eng. Pat. 8,036, May 21, 1884) proposed to improve the hardening properties of oils by adding lime and other caustic alkaline earths, and by the addition of resins similarly treated. [*Re* linseed oil, see Dieff & Reformatsky, Ber. Deut. Chem. Gesells. 20, 1211-1212; Hazura, Monatsh. Chem. 8, 260-270; Watts' Dict. Chem. 1st ed. 3, 700, 702; Allen, Comm. Org. An. 2, 'Oils'; Fox, Oil and Col. J. 4, 214, and 5, 1404; and Deering, S. C. I. 3, 541.]

Artists in oil generally use media which contain copal, amber, or some other resinous varnish, and a diluent, such as turpentine, in addition to the drying oil. A good artists' medium is composed of copal varnish, poppy oil, and a trace of white wax (Church); another medium is 'megilp,' a mixture of linseed oil and mastic varnish. Such media are, of course, added to the mixed colours by the artist.

The media for water-colour paints need no description; they are, chiefly, isinglass, size, gum-water (gum-arabic, gum-tragacanth, and gum-senegal are all used), honey, dextrine, and glycerine. Of the gums, gum-senegal is the most suitable. Dextrine is less adhesive and less brittle than gum. An alcoholic solution of honey-lævulose is preferable to honey itself.

Driers or **Siccatives.** The effect of these on the drying oils has been referred to. The driers mostly employed are litharge, acetate of lead, manganese dioxide, and manganous borate. The last-named is particularly effective: one grain of it, warmed with linseed oil, will render one ounce of the oil highly siccative (Church). Manganese oxalate, manganese linoleate, calcium borate, zinc borate, zinc oxide, zinc sulphate, burnt alum, lime, red lead, and ferric oxide are also sometimes used. White lead itself has considerable siccative power; this is one reason why it is so especially useful a pigment. The 'driers' of house-painters are commonly sold ready ground up with boiled oil. They must be used with some care, as they sometimes detract from the delicacy of the colour with which they are mixed; and for this reason the use of driers should be avoided as much as possible in paints intended for 'finishing coats.'

Paints. The mixed colours, ready for use. Common oil-paints consist of the pigments (generally white lead, with small proportions of the desired 'stainers'), ground with oil in the paint mill to a thick paste, and mixed with 'driers.' They generally require 'thinning down' with oil of turpentine to the required consistency. The oil for outdoor work is usually boiled oil; while for indoor painting pale linseed oil is frequently used, together with a larger proportion of driers. The smaller the quantity of oil used, the greater is the ultimate hardness and the less the lustre of the paint. Distemper painting, for absorbent surfaces, such as plaster, necessitates the application of a 'priming,' consisting of white lead, or, very commonly, whiting ground in water and mixed with size. There is little to specify in reference to artists' oil-paints, excepting that they consist of *pure* pigments ground in oils, no base, such as white lead, being present. Artists' water-colour paints are met with in the forms of cakes, pastilles, and tube-colours. Cakes and pastille colours are usually made by grinding the pigments into a paste with a mixture of isinglass, size, and gum-water; the paste is then compressed and dried at a moderate temperature. Such paints are ground on the palette with water before use. Tube or moist colours consist of the pigments made into a cream with honey, glycerin, &c. Church especially recommends glycerin for this purpose. [In connection with the preparation, properties, &c. of paints, see Kaiser, Mittheil. d. Bayer. Gewerb. 1885, 21—darkening of oil colours: Brousson, Eng. Pat. 4,778, Mar. 14, 1884—preservation of moist colours: Macrom, Eng. Pat. 9,414, Aug. 7, 1885—manufacture of dry colours: McClean & Smith, Eng. Pat. 11,493, Sept. 9, 1886—preparation of artists' colours: Graf, Eng. Pat. 6,844, June 5, 1885—metallic paints: Reichgesetzblatt, 11, 6—German regulations against poisonous colours: Audés, Bolley-Birnbaum's Hdbk. d. Technol., Neue Folge, Liefg. 4, 118–130—recipes for mixing common oil-paints.]

Several other kinds of paints besides those already referred to are manufactured at the present time. The principal of these are the luminous, fireproof, waterproof, anti-corrosive, and enamel paints; their composition is very varied, and space will only permit of a few short notes in reference to them.

Luminous paints contain phosphorescent alkaline earthy sulphides, combined with suitable pigments and media. Schatte, of Dresden, has succeeded in making luminous paints of many different tints (Eng. Pat. 4,732, Oct. 4, 1882). Balmain's luminous paint is a well-known preparation of this kind [*v.* E. Becquerel, On the Preparation of Phosphorescent Sulphides of Calcium and Strontium, C. R. 107, 892–894].

Fire-proof paints. These paints differ widely in composition, but asbestos is present in nearly all, and many contain alkaline silicates, borax, ground fluorspar, glass, and similar substances. See Kalke, Germ. Pat. 20,937, Feb. 7, 1882; Astrop and Ridgway, Eng. Pat. 3,932, Aug. 17, 1882; Keim, Germ. Pat. 21,784, June 1882; Kothes, Rep. Anal. Chem. 3,159; Iron, Jan. 20, 1882; Meyer, Chem. News, 48, 164; C. J. 256, 379; and d. Coninck, Eng. Pat. 3,795, Mar. 12, 1888. A mixture of aluminium and sodium silicates is sold under the name of 'fireproof cyanite.'

Water-proof paints. Lime, crushed flint and marble, sawdust, shellac, residues from petroleum-distillation, and numerous other ingredients enter into the composition of these preparations, either in addition to, or instead of, the ordinary constituents of paint. See Marck, D. P. J. 239,401; Resenscheck, Germ. Pat. 16,094, Oct. 1880; Haase, Germ. pat. 17,847, Aug. 1881; Siebel, Germ. Pat. 18,987, Dec. 1881; Gehring, Germ. Pat. 19,298, Nov. 1881; 20,725, Mar. 22, 1882—palmitate of alumina, with resin and wax: Reigelmann, Germ. Pat. 19,642, Feb. 1882: Bergh, Eng. Pat. 2,896, Feb. 7, 1884: Faquet, Eng. Pat. 10,492, Sept. 4, 1885: Wendling, Eng. Pat. 1,086, Jan. 25, 1886: and Lyman, Eng. Pat. 12,632, Sept. 17, 1887.

Anti-fouling, Anti-corrosive, or **Preservative Paints,** for surfaces of iron, ships' bottoms, &c. Many of these paints contain resinous constituents, and resemble varnishes in this respect. Oxide of iron, pitch, shellac, colophony, tannin, silicates, &c., &c., are common ingredients of these compositions. See Horst, Germ. Pat. 19,217, Jan. 1882: Wells, Eng. Pat. 3,790, May 9, 1882: Dubois, Eng. Pat. 3,320, July 4, 1883: McIntosh & Croudace, Eng. Pat. 5,330, Nov. 12, 1883: Andrews and Sutton, Eng. Pat. 5,996, Apl. 5, 1884: Brydson, Eng. Pat. 9,105, June 17, 1884: Wilmer and Bolas, Eng. Pat. 10,624, July 26, 1884: Gisborne, Eng. Pat. 312, Jan. 9, 1885: Perkins, Eng. Pat. 8,737, July 20, 1885; 7,524, May 25, 1887: Denniston, Eng. Pat. 4,415, Apl. 9, 1885: Pointon, Eng. Pat. 13,159, Oct. 31, 1885: Carter, Eng. Pat. 15,561, Nov. 29, 1886: Hannay, Eng. Pat. 12,499, Oct. 2, 1886: Cameron, Eng. Pat. 7,497, June 4, 1886: Jeyes, Eng. Pat. 2,457; Feb. 1887: Molyneux, Eng. Pat. 6,582, May 4, 1887: Wallace and Ward, Eng. Pat. 1,101, Jan. 24, 1888: Wailes and Dove, Eng. Pat. 6,012, April 23, 1888: Binns and Paris, Eng. Pat. 17,946, Dec. 8, 1888: Mullard, Eng. Pat. 20,707, Dec. 24, 1889: also D. P. J. 255 [1] 48—Dutch Railway Company's experiments, showing that red lead was preferable, as a coating for iron bridges, to any oxide of iron used; and S. C. I. 7, 48.—Report of American Navy Department on various anti-fouling paints; conclusion arrived at that pure zinc white constituted the best coating for vessels' bottoms, and that a mixture of red lead and white lead was the next best covering.

Enamel paints. These are decorative paints of brilliant colours, yielding smooth and lustrous coatings. There are many in the market at the present time, such as the Foo-Chow Enamels, Aspinall's Enamels, &c. [For manufacture, see

Fisher, Eng. Pat. 5,878, April 20, 1888, and Barnes, Eng. Pat. 764, Jan. 15, 1890.]

[*Additional references.*—Paints, pigments, methods of painting, &c.: Fremy's Encycl. Chim. tom. 10, 1888; Wagner's Chem. Techn. ed. Crookes, 1872; Field's Chromatography, ed. Salter, 1869; Riffault and others, A Practical Treatise on the Manufacture of Colours for Painting, ed. Malepyre, 1875: Standage, The Artist's Manual of Pigments, 1886; Cooley's Cyclop. Pract. Rec. ed. Tuson, 1880; Tomlinson's Cyclop. Usef. Arts, 1866.] F. G. C.

PAINT, LUMINOUS. *Barium sulphide v.* Barium, also Paints.

PALATINE ORANGE. This colouring matter is the ammonium salt of tetranitro-γ-diphenol. It is soluble in water, and dyes wool and silk orange in a bath acidulated with acetic or sulphuric acid (Hummel, Dyeing of Textile Fabrics (1885), p. 401).

Tetranitro-γ-diphenol $C_{12}H_4(NO_2)_4(OH)_2$ is obtained by the action of fuming nitric acid on γ-diphenol or on benzidine, and melts at 220°; prolonged heating with concentrated nitric acid converts it into picric acid and oxalic acid (Schmidt and Schultz, A. 207, 335).

PALISANDER WOOD. A red dyewood obtained from Madagascar, somewhat resembling sandal wood. The name is employed on the Continent as a synonym for rosewood. In the work of Bergeron a kind of striped ebony is figured as *bois de Palixandre*; in other French works this name is considered a synonym of *bois violet*, and the wood is stated to be brought by the Dutch from their South American colonies (Holtzapffel). It is said to be derived from *Jacaranda brasiliana*, Pers.

PALLADIUM *v.* Platinum metals.

PALMITIC ACID *v.* Fatty acids.

PALMITIN *v.* Fatty acids.

PALM OIL *v.* Oils.

PALM SUGAR or **DATE-TREE SUGAR.** The liquid extract of certain palms is more or less rich in saccharine substances which are easily separated from such liquids. A method of obtaining sugar from this extract has existed in India from time immemorial, and was found to prevail among the aborigines of America on the discovery of that continent.

The palms which supply sugar are *Borassus flabelliformis*, *Phœnix sylvestris*, *Caryota urens*, *Saguerus saccharifer*, &c.

Palm sugar is hygroscopic, and appears to be purgative if freely used. To divest it of this property it requires to be refined. The juice is obtained by cutting off the lower leaves of the crown about the end of October, and stripping the trunk of such as grow upon it to the place where incision is to be made. A bamboo cane is placed at the orifice each evening, by means of which the sap is conducted into vessels which are removed early next morning. The process of extracting the sugar from the sap must be proceeded with without delay, as fermentation sets in rapidly, when it is impossible to procure by boiling the syrup or *goor*, *i.e.* the mixture of molasses and crystallised sugar from which the sugar is extracted. The amount of sugar produced is about 40 p.c. of the syrup.

PALM WAX is obtained from *Ceroxylon andicola*, indigenous to the West Indies and the Andes of America; *Copernicia cerifera*, indigenous to Brazil; and *Klopstockia cerifera*, indigenous to New Grenada.

The trunks of these palms secrete the resinous wax, which, when scraped off, forms a greyish powder, the leaves also carrying a thinner layer of the same material. The wax thus obtained is melted into a compact mass over an open fire and purified by remelting. It may also be collected by boiling the bark in water, whereby the wax is softened without melting, and some of its impurities are left in the water. Kerchove de Denterghem (Les Palmiers, p. 281–282) says that the dried leaves of *Ceroxylon andicola* are beaten together and the wax detached by that means. He estimates the produce of the entire adult tree at an average of ten kilogrammes.

Palm wax is of a yellowish colour; it is hard and brittle, and breaks with a conchoidal fracture. Both the crude and the purified wax have a sp.gr. of 0·992 to 0·995, and, though they become soft by the heat of the hand, melt only at 101° to 104°.

Palm wax is a mixture of one-third wax and two-thirds resin, which may be separated by dissolving in boiling alcohol, the wax appearing as a white and somewhat crystalline jelly. By repeated treatment with boiling alcohol the resin is entirely eliminated and a pure wax resembling bee's-wax remains. The pure wax melts at 71° to a slightly yellow liquid. It is used (mixed with tallow to reduce its brittleness) for the manufacture of candles and wax varnishes.

Carnaüba wax is obtained from *Corypha cerifera*, the carnaüba palm, on the leaves of which it is secreted. It resembles other palm products in hardness, is tasteless and inodorous except when fresh. It then has a smell resembling that of new-mown hay. Its colour is a greenish-yellow; its sp.gr. is 0·995 to 0·999, and when fresh it melts at 85° to 86°; old wax melting at 90° to 91°. It is partly soluble in cold alcohol, but completely so in boiling alcohol and in ether. The concentrated solutions congeal on cooling, separating a white crystallisable mass which melts at 105°. Carnaüba wax acquires a reddish colour by boiling with potash lye, and is only partially and with difficulty saponified with alcoholic potash lye. It consists of *myricyl alcohol* $C_{30}H_{62}O$, *ceryl alcohol* $C_{27}H_{56}O$, and *cerotic acid* $C_{27}H_{54}O_2$, besides an undetermined quantity of resin.

PALM RESIN or **CEROXYLIN** *v.* Resins.

PANCLASTITE *v.* Explosives.

PAPAIN or **PAPAYOTIN.** A vegetable digestive ferment obtained from the unripe fruit of *Carica papaya*, or papaw tree, and used as an alternate to pepsin, from which it differs by being active in neutral and alkaline conditions (*v.* E. J. Easter, Ph. 1885, 45). The half-ripe fruit when scratched exudes a large quantity of a milky juice, which when dry forms a powder somewhat resembling gum arabic. The name 'papain' is usually restricted to the pure ferment associated with a proteid substance, and is obtained by precipitation with alcohol and separation of albuminous matter by basic lead acetate. The fruit of the papaw tree has long been used in the West Indies to render beef tender. The unripe fruit is split open and rubbed over the surface of the meat previous to cooking. Its action probably depends upon the fact that papain has a digestive action, not only upon muscular fibre, but also upon connective tissue. It digests fibrin and albumin in neutral and slightly alkaline solutions. When injected into the circulation in large doses it paralyses the heart. In smaller quantities it appears to favour the multiplication of micrococci in the blood (T. Lauder Brunton, Pharmacology, &c., 927).

PAPAVERINE *v.* VEGETO-ALKALOIDS.

PAPAVEROSINE *v.* VEGETO-ALKALOIDS.

PAPER. The art of modern paper-making consists in uniting or 'felting' together any fibrous vegetable matter, so as to form a continuous sheet. Owing to the abolition of the paper duties, in 1827, and the consequent rapid growth of cheap literature, the old dictionary definition of paper as 'a substance made of linen or cotton rags' no longer holds good. As a matter of fact, these substances constitute but a small fraction of the raw materials of the paper-maker.

Any vegetable substance possessing a sufficiently fibrous structure can be utilised. Occasionally both animal and mineral fibrous substances—such as wool, silk, or asbestos—are employed, either alone or as admixtures.

In order to give some idea of the variety of materials from which paper can be or has been manufactured, we may cite a book that was published at Regensburg, Germany, by Jacob Schaeffer in 1765, the paper of which was made from about sixty different sources, amongst which the following are curious and interesting: sawdust, hop-vines, hornets' nests, peat, straw, cabbage stumps, moss, various woods, thistle-stalks. In the majority of cases the paper is of very inferior quality, the pulp being coarse and unbleached. A similar book is that containing the poems of the Marquis de Villette, published in 1786. Another, of historical interest, is one the paper of which was made entirely from straw. It was published in England in 1800.

Notwithstanding the variety of materials available, rags of various kinds continued to form the chief raw material of the paper-maker until the year 1860, when Mr. Thomas Routledge introduced esparto grass (*v.* ESPARTO). This material, which possesses many advantages, is very extensively used in this country. Of late years, however, owing to the enormous increase in the demand for paper, it has been largely supplemented by straw, and more especially by wood.

The chemical characteristics of the paper-makers' raw materials have already been discussed in the article CELLULOSE. They consist, with the exception of cotton and linen rags, of one or other, or a mixture, of the various compound celluloses; and the treatment they undergo consists essentially in isolating the cellulose by chemical means. This treatment is accompanied by separation, more or less complete, into individual cells, which vary in length from about 1·5 mm. in the case of esparto to 30 mm. in the case of flax. This chemical splitting up into cells is supplemented by a mechanical operation known as 'beating,' whereby the material is still further reduced (*v. infra*).

The various processes that the different forms of cellulose undergo before being made into paper may be divided into four main branches—(1) cleaning, (2) boiling, (3) bleaching, (4) beating, or reducing to pulp. In addition to these, there are the processes of sizing, colouring, &c., which will be included in No. 4.

1. **Cleaning**. This is a purely mechanical process, and consists in removing from the raw material adventitious matter, such as sand, dirt, &c. Part of this work is done by hand-labour, especially in the case of rags, but the modern tendency is to replace hand-labour as much as possible by machinery. In the case of rags cut by machinery, the pieces, spread on to a table made of coarse wire gauze, are examined by girls, and such articles as buttons carefully removed. At the same time the rags are sorted into various kinds, such as cotton, linen, jute, canvas, &c., each kind being separately stored in boxes. This process, which is somewhat costly, is only practised in the case of rags intended to be used for high-class paper. The usual plan, which may also supplement the hand-labour, is to pass the cut rags through a 'willow.' This consists of two wrought-iron drums, furnished with teeth, which, when the drums revolve, pass rapidly near stationary teeth fixed in the frame in which the drums work. The sides and top are covered in with iron doors, and underneath is a grating for the escape of dust. The rags are fed into the drums by an endless travelling platform, and pass from thence into a duster, consisting of a kind of hollow cylinder made of iron bars covered with wire cloth. The cylinder revolves almost horizontally, a slight dip being given to it in order that the rags may be carried forward to the lower end. The 'willows' used for esparto and various other fibres are similar in principle. The cleaned and dusted rags, or other material, are carried forward by an endless felt to the boilers, where the next operation is performed.

2. **Boiling**. The boiling processes vary considerably with the kind of material. We will discuss them in the order of their simplicity.

(*a*) *Rag boiling*. Rags, being for the most part refuse from textiles made from pure or nearly pure cellulose, require a comparatively light treatment. It may be conducted either in spherical or cylindrical boilers, or in the 'vomiting' boilers, described under ESPARTO. In the case of spherical boilers the heating is caused by 'live' steam: cylindrical boilers are usually jacketed. It is preferable to cause the boilers to revolve. They are furnished with inlet and outlet steam-pipes, pipes for running in liquor and water, man-holes for filling and emptying, and safety valves, pressure gauges, &c. The alkali employed may be either caustic soda, caustic lime, sodium carbonate, or a mixture of the latter. The proportion of alkali depends mainly on the state of the rags and the nature of the substances to be removed, and also to some extent on the pressure of steam employed and the duration of the operation. As a general rule applicable to rags and all other fibres, it may be stated that the higher the pressure and the longer the time occupied, the less alkali (within, of course, certain limits) necessary to be used. The amount of alkali varies from 1 p.c. of 60 p.c. caustic in the case of the higher qualities of rags to 5 p.c. in the case of lower qualities.

The pressure also varies considerably—say, from 10 to 40 lbs. per square inch. In the opinion of some the lower pressures are to be preferred, as at the high temperature associated with higher pressure there is a tendency to fix a certain amount of dirt and colouring matter in the rags, thereby defeating to some extent the object of the boiling. After boiling, the rags may be washed in the boiler or in a separate washing engine which will be subsequently described.

A new method of boiling rags has lately been introduced with success, effecting a great economy of soda, time, and labour, at the same time producing a superior result. It consists in exposing the rags, continuously wetted with caustic soda solution, to an atmosphere of steam at 10 lbs. pressure. The dry and dusted rags are packed into waggons, fitted with perforated bottoms. The waggons are then run into a horizontal cylindrical vessel, called a 'kier,' which they almost completely fill. When in position, a pipe at the bottom of each waggon fits tightly over a pipe passing through the bottom of the kier and connected by means of a centrifugal pump with an outside pipe communicating with the top of the kier. Caustic soda solution is run in, and is made to circulate through the rags by means of the pump. One end of the kier is closed and the other is fitted with a V-shaped door, which falls into a slot of similar shape, making a readily-adjusted steam-tight joint. The door is raised and lowered by hydraulic pressure. The apparatus is known as the 'Mather Steamer Kier.'

(*b*) *Esparto boiling.* Esparto, being a compound cellulose, requires a more drastic treatment than rags. The first process that esparto undergoes is that of 'picking.' This operation, which is done by hand, consists in removing root-ends, weeds, &c. It has latterly been largely dispensed with, and a more complete mechanical treatment substituted. For this purpose the grass is passed through a willow and duster similar in principle to that described under the head of Rags.

After passing through the machine the grass is in some cases carried along a travelling felt, and is discharged direct into the boiler. These are almost invariably stationary, as a revolving boiler is apt to cause the grass to form into dense masses, which resist the action of the soda used in boiling. An esparto boiler is shown in fig. 1. It is furnished with a perforated false bottom B, on which the grass rests. Steam enters by the pipe A, which reaches below the false bottom and causes the liquor to rise up the outer pipe C, strike against the 'bonnet' D, and distribute itself over the grass in a fine spray. The door E is for filling in the grass, and the door H for emptying. The boiler is fitted with a safety valve K. Each boiler holds about 30 cwt. of grass, and the operation lasts about five hours. The amount of soda varies according to the nature of the esparto, Spanish requiring less than African: about 16 lbs. of 60 p.c. caustic per cwt. is an average quantity. The steam pressure also varies from 5 lbs. to 45 lbs. per square inch, occasionally an open boil is used. The modern tendency is to employ the higher pressures, as being more economical of time and soda. Other forms of vomiting boilers have lately been introduced, in which the vomiting arrangements are fixed either outside the boiler altogether, as in Roeckner's, or are placed at the sides, as in Sinclair's, thus giving more space for the grass. The alkali used is invariably soda. The boiling operation being completed, the liquor is run off from a cock at the bottom of the boiler, and the grass partially washed with water in the boiler. This also has the effect of cooling the grass and enabling the workmen to remove it to the washing engine or 'breaker.'

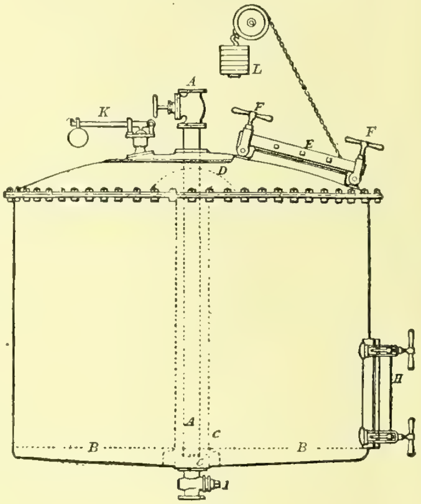

FIG. 1.

In some mills the grass is placed in a series of tanks similar to those used for dissolving black ash, where the washing can be effected with a very small quantity of water—a very important matter from the point of view of recovery of the soda.

The washing engine, which may be used for any other fibre besides esparto, is shown in fig. 2. It consists of a rectangular vessel with rounded ends, in the centre of which is the mid-feather B. The action of the roll A, which is fitted with clusters of steel knives G, disintegrates the grass and causes it to circulate round the engine. The floor is sloped as shown by the dotted lines D and D′, the effect being to cause the grass to pass under the roll A, the knives of which pass close to similar stationary knives fixed to the 'bed-plate' I. The distance between the roll and the 'bed-plate' can be varied at will by means of the wheel E.

A continuous stream of water is run into the engine, and the dirty water is lifted by means of the 'drum washer' C, the periphery of which is covered with fine wire gauze. The centre of the drum is formed of a conical tube, the narrow end of which is towards the 'mid-feather.' The dirty water passing through the wire gauze is lifted by the bucket-like compartments C, and is discharged through the centre of the drum, whence it is led away by the trough L, and passes down the 'mid-feather,' which is made hollow for the purpose.

The grass having been thoroughly washed and reduced to the state of pulp by means of the steel knives in the roll, is ready for bleaching. This operation will be described subsequently.

(*c*) *Straw boiling.* Straw closely resembles esparto in its chemical characteristics, but being more highly lignified a somewhat severer treatment is required. This is obtained either by boiling at a very high pressure, 60–80 lbs., or by using a larger proportion of caustic soda (18–20 lbs. per cwt.). In treating straw for use in high-class papers, it is necessary to boil under such conditions that even the knots, which are much less readily attacked than the bulk of the straw, shall be so far acted upon that they may be easily bleached. This treatment causes a diminished yield of pulp and a somewhat weakened fibre. For inferior papers such care is not necessary, and a less severe treatment suffices. An excellent method of cleaning straw preparatory to boiling consists in forcing the straw, previously cut into fragments of about 1–2 inches in length, along a tube into a chamber, the sides of which are made of wire gauze, which allows the dust and dirt to escape.

The boiling operation is usually conducted in large revolving boilers. Owing to the rotary action of the boiler, the straw is in the state of fine pulp and readily flows through a 3-inch pipe. It is run into tanks, the bottoms of which are formed of perforated tiles. The liquor is run off and fresh water added until all soluble matters have been removed. It is then ready for bleaching.

In making straw pulp of fine quality it is sometimes found advantageous to pass the washed pulp between horizontal revolving stones, whereby the knots and any unboiled portions are finely ground and rendered more easily bleached.

(*d*) *Wood v.* CELLULOSE.

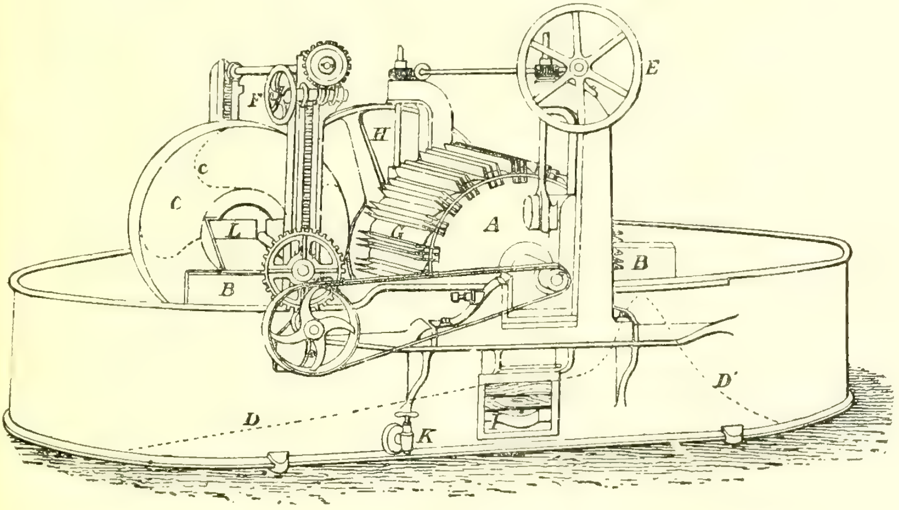

FIG. 2.

(*e*) *Other fibres.* There are a number of fibrous materials which are available for the paper-maker, such as jute, manilla, adansonia, &c., the treatment of which calls for no special notice. The nature of the treatment which they undergo varies with the kind of paper for which they are intended. The greater number of such fibrous materials are used for papers where strength is of far greater importance than colour or appearance, such, for example, as brown papers and packing papers. In such cases the paper-makers aim at a minimum resolution of the fibre, so as to preserve the strength and increase the yield. In the case of jute the individual fibres are very short and weak, and a strong and perfectly white paper made from jute is an impossibility. If, however, the filaments are not completely resolved, a strong fibre can be obtained.

The cheapest method of preparing such fibres is to boil them under pressure with milk of lime. This treatment is not nearly so effective as that with caustic soda, and the fibre produced is coarse and hard. The yield is, however, high.

There is another very important material which may be mentioned here, viz., mechanical wood-pulp. A large quantity of this is used in the cheaper kinds of paper. It is prepared by disintegrating wood by mechanical means alone. Blocks of wood, from which the knots have been removed, are pressed against revolving stones; at the same time a stream of water flows on to the stones. The wood is so placed that the fibres are torn off in the direction of their length in order to secure as great length as possible. The stream of water carries the pulp forward as fast as it is made. The larger undisintegrated portions are removed by screens of coarse wire cloth. In order to still further refine the pulp it is caused to pass between two horizontal cylinders of sandstone, the upper one of which revolves rapidly.

Where power is cheap such pulp can be economically prepared; it is, however, at best but a poor substitute for esparto and other pulps. Paper made with it has but little strength, and is very susceptible to atmospheric action. The woods chiefly used are white pine and aspen; the latter yields a pulp of good colour but little strength.

3. **Bleaching.** The processes of bleaching paper-pulp are practically identical for all classes of material. The agent employed is a solution of calcium hypochlorite, made by dissolving bleaching-powder in water. The operation may be conducted in the breaking engine previously described, or in a separate engine called a 'potcher,' which is similar in construction, but the roll is furnished only with blunt blades which serve as paddles to cause the pulp to circulate. Sometimes large potchers made of brick and cement are used.

The action of the calcium hypochlorite may be hastened by heat, the 'potchers' being provided with steam pipes for this purpose, or by the addition of sulphuric or hydrochloric acids. The best results are obtained by the action of bleaching solution alone, in which case a longer time must be given. This is more than compensated for by the extra yield of pulp and its greater strength.

The amount of bleaching-powder necessary to bleach well-boiled pulps varies from about 7 p.c. in the case of straw to about 15 p.c. in the case of wood. These amounts are calculated on the unboiled materials.

Chlorine gas as a bleaching agent was formerly used for rags, but is now almost entirely superseded. As a matter of fact, chlorine will not bleach the majority of pulps; it enters into combination with the fibre substances, producing yellow-coloured combination products. Advantage has been taken of this fact by F. C. Glaser in his process for treating straw. The straw is first boiled with a reduced quantity of soda; it is then drained and exposed to the action of chlorine gas. A subsequent treatment with bleaching liquor produces a very pure white pulp.

The bleaching of pulp by means of the products of the electrolysis of chlorides has lately attracted much attention. Of the various processes introduced, the best known is that of M. Hermite, which is in successful operation in many mills on the Continent. It depends upon the fact that when a solution of magnesium chloride is electrolysed, magnesium hypochlorite is formed, which possesses considerably greater bleaching efficiency than calcium hypochlorite of equal chlorine strength.

After bleaching, and before the next operation of beating, the pulp is sometimes purified by passing it over a 'presse-pâte,' which consists of a strainer and that part of a paper machine on which the web of paper is formed. The pulp is thus made into a thick continuous sheet; at the same time all soluble impurities, such as calcium chloride, &c., are removed.

4. **Beating.** The bleached pulp, before being made into paper, requires to be beaten up into fragments of from 1–2 mm. in length. In the case of esparto, straw, and wood, this length represents that of the individual fibres; the beating operation, therefore, is confined to completing the disintegration produced by the boiling and bleaching processes. But in the case of cotton and flax, the individual fibres of which are about 30 mm. in length, a much more extended mechanical treatment is necessary. The operation is conducted in an engine called the 'beating engine,' similar in construction to the breaking or washing engine already described (fig. 2), the only important difference being that the roll of the former is furnished with a larger number of knives.

The distance between the roll and the bedplate is arranged so as to 'tear' the fibres, instead of 'cutting' them, so as to give them the maximum amount of felting power. In some cases the knives are made of bronze in order to avoid contamination of the paper with iron-rust. Various other forms of beating engines have lately been introduced which differ somewhat in the arrangement of the various parts, but which do not call for special notice.

It is in this stage of the treatment of the pulp that the various loading, sizing, and colouring materials are added. Before doing this, however, it is necessary, unless the operation has been previously performed in the washing engine, to remove the excess of bleaching solution. This may be done by simple washing, many beating engines being provided with washing drums for the purpose; or the bleach may be neutralised by the addition of an antichlor, such as sodium thiosulphate or sodium sulphite.

5. **Loading.** Most papers, except perhaps the very finest 'writings,' contain some added mineral matter, such as 'pearl-hardening' (calcium sulphate, ground or precipitated) for the better qualities, and china clay for the cheaper papers. This addition cannot, unless carried to excess, be considered an adulteration, as it fills up the pores of the paper, and enables it to take a better surface under the calender.

Sizing. All writing papers, and most printing papers, require to have some material added to them that will enable them to resist ink. This can be done in two ways—viz., by engine-sizing and tub-sizing: the former is done in the engine itself, the other in the finished paper. Engine-sizing consists in the addition of resinate of alumina, which is precipitated in the pulp by the mutual decomposition of resinate of soda, prepared by dissolving rosin (colophony) in sodium carbonate, with a solution of alum or aluminium sulphate. In addition to the resinate of alumina most papers contain starch, which may be dissolved in water and mixed with the resinate of soda, or may be added undissolved: the former is the plan usually adopted. Almost all papers, even blotting papers, contain starch, it assists in binding the fibres together, but has little or no sizing property, and therefore does not prevent the paper being absorbent. The amount of alum added to pulp is largely in excess of that necessary to fully precipitate the resin; the excess appears to be necessary in order to get a hard paper. It probably has some action on the cellulose itself. The excess, moreover, tends to brighten the colour of the paper.

Tub-sizing. This consists in passing the finished paper, either in the form of sheets or in the web, through a solution of gelatine to which alum has been added. In some cases soap is added to the gelatine. When alum is added to a solution of soap and gelatine, the soap is decomposed and an infinitely fine precipitate is produced, which forms with the gelatine a kind of emulsion. The addition of the soap enables the paper to take a high surface with a minimum of pressure under the calender.

6. **Colouring.** Most bleached pulps have a slight yellow tinge which requires to be complemented by the addition of blue and pink in order to produce a perfectly white paper. The blues usually employed for this purpose are ultramarine and smalts, and occasionally aniline blues; the pinks are either preparations of cochineal or aniline. For the production of coloured papers a variety of different colouring matters are employed in addition to those mentioned, such as Prussian blue, chrome yellow, Venetian red, &c.

The addition of the loading, sizing, and colouring materials proceeds at the same time that the pulp is being 'beaten.' When this is completed the pulp is ready to be made into paper.

7. **Making into paper** (*Hand-made paper*). This is made on a mould of wire-cloth, furnished with a moveable frame of wood called a 'deckle,' extending some distance above the surface. The workman dips the mould with its 'deckle' into a vat containing the beaten pulp largely diluted with water, and removes more or less pulp, according to the thickness of paper required. He, then, by dexterous lateral movements causes the fibres to unite and form a continuous sheet; at the same time the excess of water drains away. The 'deckle' is then removed, and the wet sheet of paper transferred to a piece of felt. This operation is continued until a number of sheets of paper and pieces of felt have accumulated. They are placed in a press to remove a further quantity of water. The sheets are then passed through a solution of gelatine, and hung up on lines or poles to dry. When dry the sheets are calendered.

Comparatively little paper is now made by hand on account of the great expense of labour; it is, however, preferred for bank-notes, drawing-paper, &c., on account of its uniform strength. Owing to the fact that a shaking motion in every direction can be given to the mould, the fibres are irregularly distributed, and the maximum of felting power is obtained, whereas in machine-made paper, as will be seen subsequently, the fibres tend to place themselves in the direction in which the stream of pulp flows. Such paper, therefore, is strongest across the web.

Machine-made Paper.

The modern Fourdrinier paper machine, so-called from the original inventor, consists essentially of an endless mould of wire-cloth on to which a continuous stream of pulp flows and on which a continuous sheet of paper is formed. On leaving the wire-cloth the wet sheet of paper passes through a series of rollers and over heated cylinders and calenders whereby it is dried and finished. The machine is shown in side elevation figs. 3 and 4.

The pulp on leaving the beaters flows into a large store vessel called a stuff-chest where it is diluted to the proper consistency with water. It is furnished with agitators to keep the pulp uniformly distributed. From here it is pumped and delivered under a constant head, to the sand tables. These consist of a long series of shallow troughs, the bottoms of which are covered with pieces of felt or thin strips of wood placed across the direction of the stream of pulp and at a slight angle, the object of which is to retain any particles of sand or dirt. The pulp passes from the sand tables to the strainers, which consist of strong bronze plates having a large number of fine V-shaped slits cut in them. The slits are from 2–3 inches long, and vary in width from ·007 to ·05 of an inch. These slits allow only the fine fibres to pass, retaining all unboiled or unbleached portions of fibre or other impurities. The passage of the stream of pulp through the slits is assisted by giving a vigorous shake to the strainer plates or by means of a pump placed below. One of these strainers is shown at c; the shake is produced by the cam a acting on the hammer b.

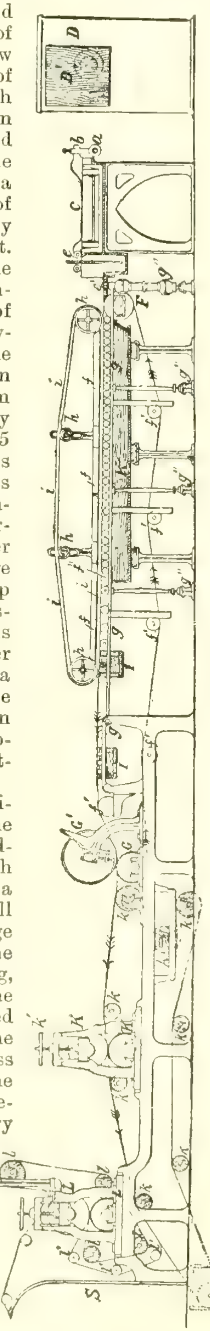

Fig. 3.

The strained and purified pulp passes from the strainer on to an endless travelling wire-cloth which is carried by a large number of small rolls f'' and by the large rolls F f' and G. The amount of pulp flowing, and consequently the thickness of the finished paper, is regulated by the sluice e. The thickness also depends upon the rate at which the wire-cloth travels; it may vary from 60 to 270 feet per minute.

Travelling with the wire-cloth are two endless thick india-rubber bands i called 'deckle straps.' These can be regulated at any distance from each other and serve to determine the width of the sheet of paper. The rolls f'' and the wire-cloth are carried by standards g'' which are jointed at their lower ends. At the top they are connected with a rod having a rapid to-and-fro motion which is communicated to the wire-cloth. This shaking motion serves to some extent to neutralise the tendency of the fibres to set themselves in the direction of the flow of the pulp.

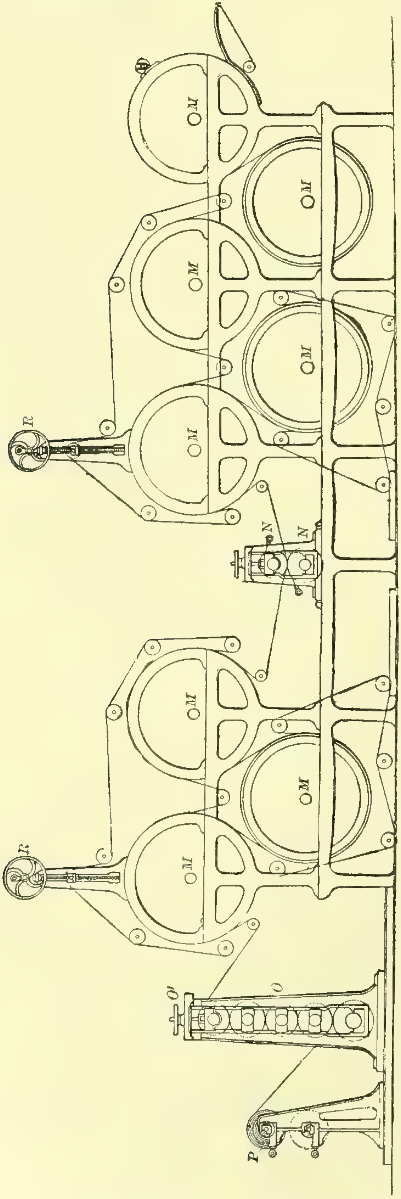

FIG. 4.

The small rolls f' cause the excess of water to pass more freely through the wire-cloth. As the sheet of paper passes along, it goes over the vacuum boxes I which are connected with air-pumps, by which a further quantity of water is removed from the sheet of paper.

Underneath the wire-cloth is a box K called a 'save-all.' The water passing into it holds in suspension a certain amount of fibre. This water is used to dilute a fresh quantity of pulp. Any pattern, or 'water-mark' as it is called, may be produced on the paper by causing a light skeleton roll, called a 'dandy roll' covered with raised wire in the form of the pattern required, to press lightly on the wet paper. It is generally placed between the vacuum boxes I. After passing the last box I the still wet paper passes between the 'couch-rolls' GG'. These are covered with felt and serve by their pressure to still further dry the paper. The paper here leaves the wire-cloth and is transferred to an endless felt which travels in the direction of the arrows over the roll *k*. On its journey it passes between the 'first-press rolls' K, and then through the 'second-press rolls' L. The paper, being still weak, is supported by a felt travelling on the rolls *l*. After leaving the 'second-press rolls' L, the paper is carried to the drying cylinders M, heated with steam, of which there may be as many as twelve or more.

They are generally divided into two sets, between the sets being a pair of highly polished heated rollers N called 'smoothers.' After leaving the last drying cylinder the paper passes through the calender O and is then wound off at P.

Single cylinder machine. In the single-cylinder or 'Yankee' machine, the paper after having been formed on a wire cloth in substantially the same manner as in the Fourdrinier machine, is dried by passing over one very large cylinder.

In another form of machine the paper is formed on the periphery of a cylinder covered with wire cloth, which revolves in a vessel containing the pulp.

Calendering. It is sometimes necessary to give a greater 'surface' to a paper than is acquired by the calender at the end of the machine. This may be done in several ways. One method, called 'web-glazing,' is to pass the web of paper between alternate rolls of polished iron and highly compressed cotton or paper. Another method called 'plate-glazing,' consists in passing a bundle of sheets of paper alternated with polished zinc or copper plates, between a pair of rolls to which great pressure is applied.

Still another method, which is known as 'friction-glazing,' is to pass the web of paper between two rolls, one of which travels at a much higher rate than the other. After calendering, the paper only requires cutting and sorting before being placed on the market.

Soda recovery. Formerly, before the introduction of the Rivers Pollution Act of 1876, all liquors in which esparto and other fibres had been boiled were thrown away; it is now the practice to recover the soda contained in them by evaporating to dryness and incinerating the residue, thus obtaining the soda in the form of carbonate. This has in most cases been found to be highly remunerative. Various forms of apparatus for economically evaporating large quantities of water have from time to time been introduced. A very effective form is that known as the Porion evaporator, which consists of a large brick chamber on the floor of which the liquor is placed. A number of rapidly revolving fanners stir up the liquor and distribute it in the form of a very fine spray. The chamber is connected with a reverberatory furnace where the evaporated liquor is incinerated, the waste heat from which serves for the preliminary evaporation. This evaporator, working with fairly strong liquors, is capable of producing 1 ton of recovered soda for an expenditure of about 27 cwt. of coal.

Several forms of multiple effect evaporators have been introduced. The first of this kind was the Chapman evaporator which resembles the ordinary vacuum pans of the sugar refiner. The Yaryan evaporator is similar in principle, but the evaporation takes place in a number of narrow tubes (*v.* EVAPORATION). An important advantage of these evaporators is the fact that the liquors, excepting while in the incinerating furnace, are not in contact with the products of combustion of the fuel employed. Moreover, the bulk of the water evaporated is recovered in the form of distilled water.

The recovered soda, which, as has been said, is in the form of carbonate, may contain in addition a considerable quantity of potash, derived from the fibrous substances which have been boiled in it; also in the case of straw or esparto, a large proportion, as high as 7 p.c., of silica. It is dissolved in water and causticised by boiling with lime, when almost the whole of the soda it contains is recovered in the form of sodium hydrate. It should be borne in mind, however, that it is liable to contain various accumulated impurities such as sulphate and chloride &c., derived from the soda originally employed, and from that which has to be added to make up the loss in evaporation. This loss, together with that due to soda retained in the fibre, leakage, and soda volatilised during calcining, that left in the lime mud after causticising, invariably amounts to 15–20 p.c.

It is important that the loss should be made up with as pure a form of alkali as possible.

E. J. B.

PAPER-COAL. A synonym for *Dysodil* (*q. v.*).

PARACETOPHENETIDINE *v.* PHENACETIN.

PARADIGITALETIN *v.* DIGITALIS.

PARAFFIN.

Manufacture of Paraffin Oil and Wax.—The manufacture of paraffin and paraffin- or coal-oil was originated by the late James Young, of Kelly, in 1851. The process essentially consists in the destructive distillation of carbonaceous minerals at a comparatively low heat. The products formed are a green oily liquid known generally as crude oil, an incondensable gas, and, as the minerals used are usually also nitrogenous, a weak ammoniacal liquor. The ammoniacal liquor is converted into any of the commercial ammoniacal compounds and the gas is used for distilling succeeding portions of the mineral. The crude oil has a sp.gr. of ·860–·890° and solidifies at ordinary temperatures. It consists of 70–80 p.c. paraffins and olefines mixed with large quantities of alkaloidal bases of the pyridine series, and smaller quantities of cresols and phenol. In refining it yields the following products in varying percentages depending on the kind of mineral and the nature of the destructive distillation to which it was subjected.

	Sp.gr.
Naphtha or shale spirit . .	·700–·740
Burning or paraffin oil . .	·800–·820
Medium or light mineral oil .	·840–·865
Heavy lubricating or mineral oil	·875–·895

Paraffin-wax or ‘Scale,’ m.p. 86-140°F.

The liquid bodies are mixtures of hydrocarbons of the paraffin and olefine series. Naphtha contains 60–70 p.c. olefines and other hydro-carbons acted on by fuming nitric acid: burning-oil, 30–80 p.c.; and the lubricating oils consist almost entirely of olefines, due probably to cracking up in the distillations necessary in refining. Fractional distillation is employed to separate the liquid bodies, and the solid paraffin, which distils over with that portion of the oil having a greater sp.gr. than ·840, is separated by cooling and crystallisation.

When the destructive distillation of carbonaceous minerals at a low heat was first commenced, a maximum yield of oil suitable for illuminating purposes was the point to be attained, and a horizontal retort similar in all respects to the present coal-gas retort was used. At that time the carbonaceous minerals used were coaly shales, more allied to Parrot coal than to the real oil shales. No shale was worked which yielded less than 40 gallons of oil per ton, and the mineral most largely used was the celebrated Torbanehill mineral. When the oil produced was refined, that portion only which had a lower sp.gr. than ·840 and which was suitable for illuminating was retained; the residue, consisting of the heavier oil and solid paraffin, was burned. Soon after the starting of the first paraffin oil works at Bathgate, in Scotland, it was discovered that these heavier oils made very suitable lubricants, and that the solid paraffin, on being refined, could be made into candles. This necessitated a change in the construction of the retort, for the horizontal retort, however well adapted for the manufacture of the lighter oils, was not fitted for the preservation of the heavy oils and paraffin, owing to the tendency of the paraffins to split up into a lower paraffin and olefine while hanging slowly about the hot sides of the retort. Young then patented the first vertical retort and introduced steam during the distillation. The improvement claimed was a better yield of crude oil of a better quality. The first vertical retort was round in shape: six retorts were set in an oven, one furnace firing them. At the bottom each retort was sealed in water and the shale was introduced at the top by a hopper closed by a bell attached to a weighted lever. Steam was introduced at the bottom to sweep the oil vapours upwards to the exit at the top. The shale travelled downwards, meeting a gradually increasing heat. So suitable was the retort that it was, until the last few years, in use in many works in Scotland, and even now the most recent retort is essentially a modification of the first vertical retort. Nearly coincident with the introduction of this retort, ammonium sulphate became an article of commerce, and the watery ammoniacal liquor which separated from the oil was converted into sulphate of ammonia. The vertical retort, owing to the introduction of steam, yielded considerably more ammonia than the horizontal.

The next improvement introduced was the destructive distillation of the shale under a slight vacuum. At first, and even still, this vacuum was produced by a steam jet blowing through a cone, but the jet is being gradually superseded by mechanical exhausters. Formerly the mixture of oily and watery ammoniacal vapours, the products of the distillation, coming from each retort, was led to separate condensers. Now it is the practice to conduct the vapours from each bench of retorts into one large condenser. These condensers are merely long ranges of pipes, usually placed vertically, and exposed as much as possible to the action of the air. In summer a spray of water may be thrown over them to assist in cooling. The crude oil and water are drawn off at the bottom of each set and separated in any suitable manner, advantage being taken of their different specific gravities.

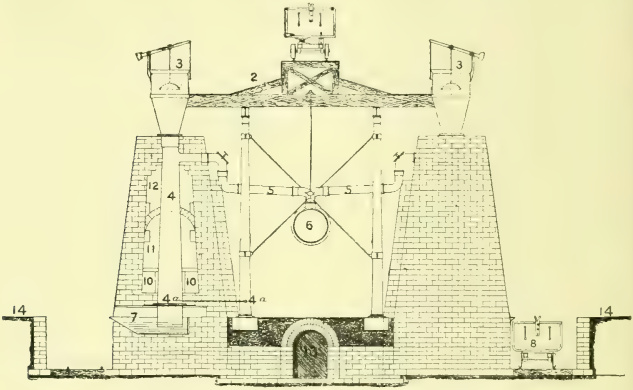

Fig. 1.—Old Vertical Retort (End elevation and section).

Description applicable to Figs. 1 and 2:—1. Charging hutch. 2. Shale platform. 3. Charging hopper. 4. Cast-iron retort. 4*a*. Retort steam pipe. 5. Gas exit. 6. Gas main. 7. Water seal for cooling spent shale. 8. Spent shale hutch. 9. Furnace. 10. Lower or bottom chamber. 11. Mid or centre chamber. 12. Top chamber and flue. 13. Main flue. 14. Retort drawing level.

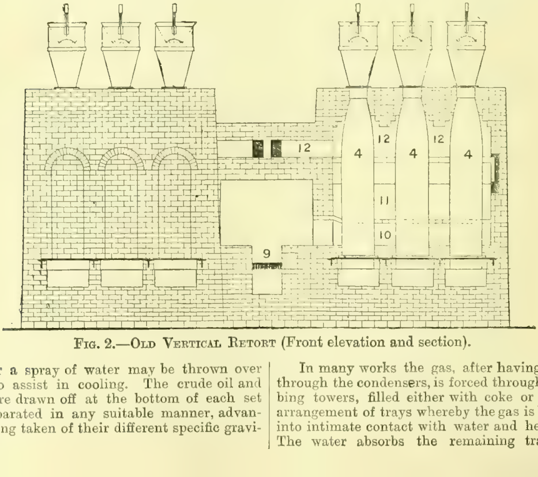

Fig. 2.—Old Vertical Retort (Front elevation and section).

In many works the gas, after having passed through the condensers, is forced through scrubbing towers, filled either with coke or with an arrangement of trays whereby the gas is brought into intimate contact with water and heavy oil. The water absorbs the remaining traces of ammonia in the gas, and the heavy oil absorbs a considerable proportion of naphtha, varying in proportion to the extent of the previous cooling, but usually amounting to 1½ to 2½ gallons per ton of shale. The heavy oil is freed from the light naphtha by steam distillation, and after cooling it is again used to absorb fresh naphtha. It has also been found that if the gas be compressed after passing through the condensers this naphtha can be obtained, but this process is much more expensive than the other.

For some years after the introduction of the vertical retort, various modifications were devised, aiming at a better quality of crude oil, a greater yield of ammonia, and cheaper working, but none were of practical importance till in 1871 William Young, of Magdalen Bridge, now of Peebles, constructed a retort to utilise as fuel the fixed carbon of the mineral after the volatile matter had been distilled. The oil, however, contained too much tar, due to an attempt to combine retort and furnace in one continuous tube, the two being separated by a gas lute, which was intended to prevent combustion spreading to the oily vapours above.

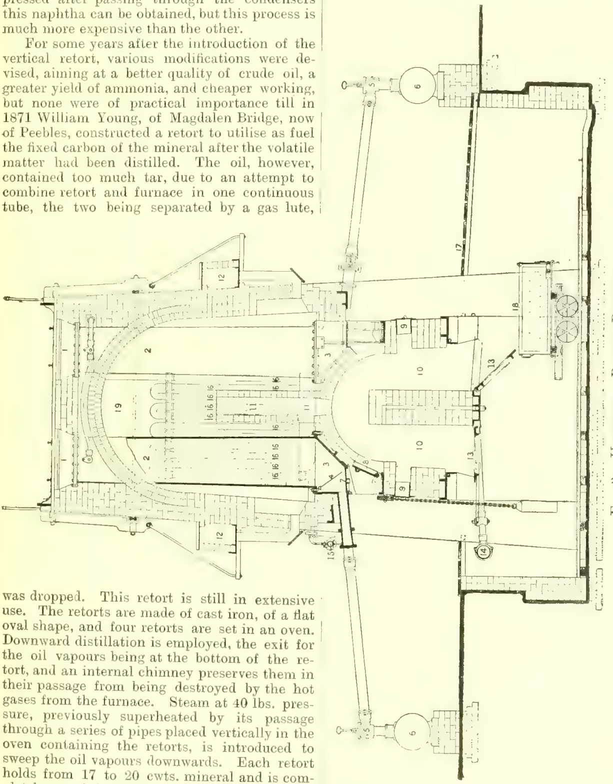

FIG. 3.—HENDERSON PATENT RETORT.

1. Charging hopper. 2. Iron retort. 3. Retort shoot. 4. Guard plate. 5. Gas valve. 6. Gas main. 7. Retort bottom door. 8. Folding door forming shoot to furnace. 9. Firing door. 10. Furnace or combustion chamber. 11. Chimney to protect retort bottom. 12. Flue. 13. Grate bars and folding door. 14. Return gas main. 15. Steam main. 16. Steam superheater. 17. Retort dropping platform. 18. Spent shale hutch. 19. Top chamber containing four retorts.

Shortly afterwards, Henderson, of Oakbank, now manager of the Broxburn Oil Company, Limited, improved upon this arrangement by constructing a retort with a separate furnace below, into which, by a neat mechanical arrangement, the mineral exhausted of volatile matter was dropped. This retort is still in extensive use. The retorts are made of cast iron, of a flat oval shape, and four retorts are set in an oven. Downward distillation is employed, the exit for the oil vapours being at the bottom of the retort, and an internal chimney preserves them in their passage from being destroyed by the hot gases from the furnace. Steam at 40 lbs. pressure, previously superheated by its passage through a series of pipes placed vertically in the oven containing the retorts, is introduced to sweep the oil vapours downwards. Each retort holds from 17 to 20 cwts. mineral and is completely emptied and filled every sixteen hours, the retorts at opposite corners of the oven being taken alternately. The furnace is divided in two, the charge from one of the retorts filling one of the divisions to the firing door. A folding door at the bottom of the furnace forms a convenient means of discharging the spent shale into the hutch below. It is found that the incondensable gas and the residual carbon of most minerals form quite sufficient fuel to keep the oven in heat, but if the mineral contain a low percentage of fixed carbon a little coal introduced through the firing door is necessary. The advantages claimed for this retort over its predecessors are (1) good quality of crude oil, due to thorough preservation of the paraffins; (2) more thorough extraction of ammoniacal compounds by the superheated steam; (3) saving in fuel; (4) saving in labour. In 1879–80 Young and Beilby simultaneously discovered that, if the shale, after complete distillation of the volatile matter, were submitted to the continued action of steam at a high temperature, an increased amount of the nitrogen of the shale was obtainable as ammonia. The oxygen of the steam combines with the residual carbon, and the nascent hydrogen forms ammonia with the remaining nitrogen. They therefore constructed a retort having two separate and distinct heats, the lower at the top for distilling the oil, the higher at the bottom aiding the combustion of the fixed carbon in a current of steam. The lower, or ammonia-making portion of these retorts, is built of brick, the higher, or oil-distilling portion, of iron, although recently the retorts portion has also been built of brick throughout. The retorts are built in ovens of eight, each oven having regulating dampers at each corner. Steam is introduced at the bottom, and that portion of it which is not decomposed in passing through the glowing carbon, along with the gases formed from that decomposition, aid in the distillation of the freshly introduced mineral above. When the shale is completely spent it is withdrawn into the hutch below in small quantities at a time, at intervals of 3 to 4 hours, fresh mineral being introduced at the top. A large hopper is placed in connection with every four retorts, through which the oil vapours pass before entering the main. The cold shale in this hopper condenses the heavier oil vapours, which are again distilled by the upward current of super-heated steam, and the oil is thus supposed to get a practical re-distillation, and consequent purification. These retorts are capable of distilling 25 to 30 cwts. per 24 hours. Each oven has two coal retorts, the gases from which aid in the heating of the oil retorts, and if desired the ammonia from the coal can be recovered. The advantages claimed are: (1) Yield of ammonia practically doubled; (2) crude oil containing less tar due to the re-distillation in the hopper; (3) cheaper labour.

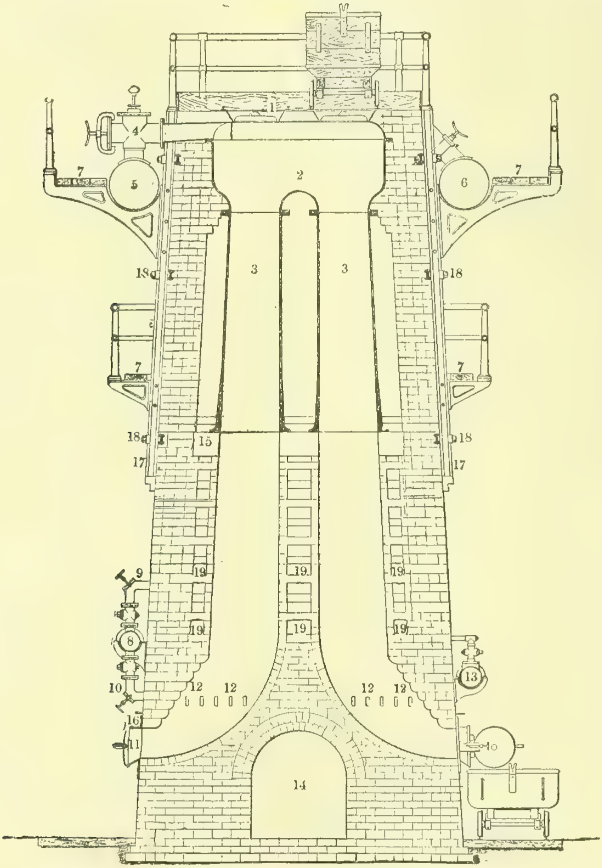

Fig. 4.—Young and Beilby Patent Retorts (Section through Shale Retort).

1. Raw shale hopper. 2. Redistillation chamber. 3. Retort. 4. Gas valve. 5. Shale gas main. 6. Coal gas main. 7. Platform. 8. Steam main. 9. Coal retort steam pipe. 10. Shale retort steam pipe. 11. Spent shale drawing door. 12. Steam chequers. 13. Return gas main. 14. Main flue. 15. Chamber flue. 16. Damper. 17. Binder rails. 18. Binding bolts. 19. Heated gas ports.

The paraffin industry is located almost entirely in Scotland, although in Southern Germany and Australia distillation of mineral for the production of crude oil is to some small extent carried on. In Scotland the minerals wrought are, with one or two exceptions, certain seams of shale lying between the coal system and the old red sandstone.

All these seams are well known and well defined in their separate characteristics of yields of oil, solid paraffin, and ammonia. These are the true paraffin shales, and are distinguished from the coaly shales which were originally wrought, by their tendency to yield under all heats whether high or low, members of the paraffin and olefine series, rather than members of the benzene group. The following are the shales at present being wrought with the yields of crude oil and sulphate of ammonia with the Henderson and Young and Beilby retorts :

—	Gallons oil per ton	Henderson $(NH_4)_2SO_4$. lbs. per ton	Y. and B. $(NH_4)_2SO_4$. lbs. per ton
Broxburn .	28–33	16–20	26–32
Fells . .	36–40	11–14	25–35
Straiton or Briderburn	26–30	5–8	20–26
Pumpherston .	16–22	25–35	50–60

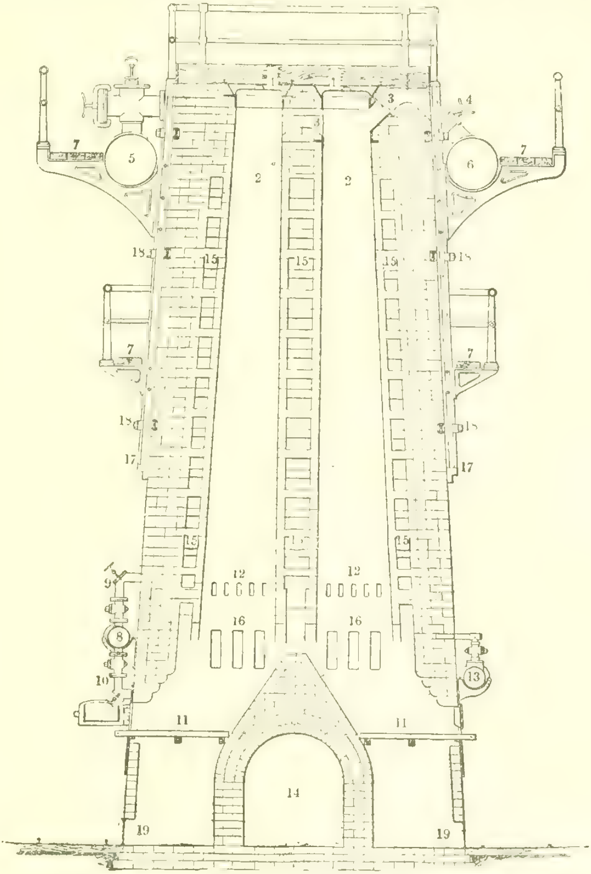

FIG. 5.—YOUNG AND BEILBY PATENT RETORT (Section through Coal Retort).

1. Coal retort hopper. 2. Coal retort. 3. Gas exit. 4. Coal gas valve. 5. Shale gas main. 6. Coal gas main. 7. Platform. 8. Steam main. 9. Coal retort steam pipe. 10. Shale retort steam pipe. 11. Furnace. 12. Steam chequers. 13. Return gas main. 14. Main flue. 15. Heated gas ports. 16. Heated gas exits from furnace. 17. Binder rails. 18. Binder bolts. 19. Furnace ashpit dampers.

From the tanks at the retorts the crude oil is conveyed to the refinery. Here it is subjected to repeated distillation, and treatments with acid and soda. The preservation of the paraffins from 'cracking up' during distillation, and of the olefines from formation of sulpho-olefine compounds during the treatment with sulphuric acid, forms the basis of the most approved methods of refining crude oil. The process varies in different works, and with different oils and with market prices.

Distillation is usually conducted in large stills similar to that shown in section (Figs. 6 and 7). The bottom is of cast iron, the top or body of malleable iron. Those holding 2,000–2,500 gallons are now in most general use, having superseded stills of a smaller size. Each still is fitted with a 'feed pipe' for charging, a 'dip pipe' for ascertaining the contents during distillation, and a steam pipe for introducing steam at from 10–40 lbs. pressure. The introduction of steam keeps the oil in constant ebullition and from clinging about the hot bottom of the still, and helps to preserve the paraffins from degradation. The exit from each still is connected with a suitable water condenser, containing 230 ft. 4 in. cast-iron pipe. If it be a still used for fractional distillation, pipes connected with different tanks receive the various fractions. Before passing to the tanks the steam water requires to be separated. This is very expeditiously done by means of 'separators,' consisting of oblong boxes, with two outlets on nearly the same level, although one connects with the bottom. When the mixture of oil and water enters the 'separator' the water settles to the bottom and escapes by one pipe, while the oil is skimmed from the top by the other.

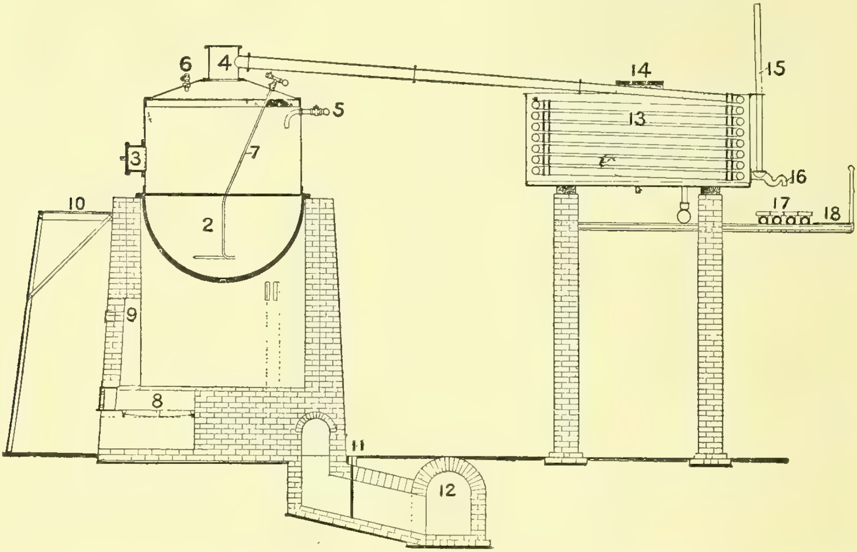

Fig. 6.—Section Still and Condenser (2,000 gals. capacity).

Description applicable to Figs. 6 and 7 :—1. Malleable iron still top. 2. Cast iron still bottom. 3. Manhole and door 4. Dome and gas exit to condenser. 5. Oil feed or charging pipe. 6. Dip cock. 7. Steam pipe. 8. Furnace. 9. Spy box. 10 Cleaning platform. 11. Damper. 12. Main flue. 13. Condenser. 14. Platform for feedwater cocks to condenser. 15. Incondensible gas exit pipe. 16. Oil exit, or worm end. 17. Oil receiving pipes. 18. Platform for worm ends.

In an ordinary distillation the still is charged from a tank on a higher level to within 18–24 in. from the top, to allow room for expansion ; fire is then applied below. In a few hours the still begins to boil, and water appears at the worm, and with it a little of the lighter oils. After the water is completely driven off, which will be in ten to twelve hours, steam is introduced in gradually increasing volume during the distillation, until, when the heavier oils are being distilled, from 15 to 25 p.c. water is coming over with the oil. The oil is distilled to dryness, the residue being coke. The time taken to fire a 2,500 gallon still from the starting of firing to

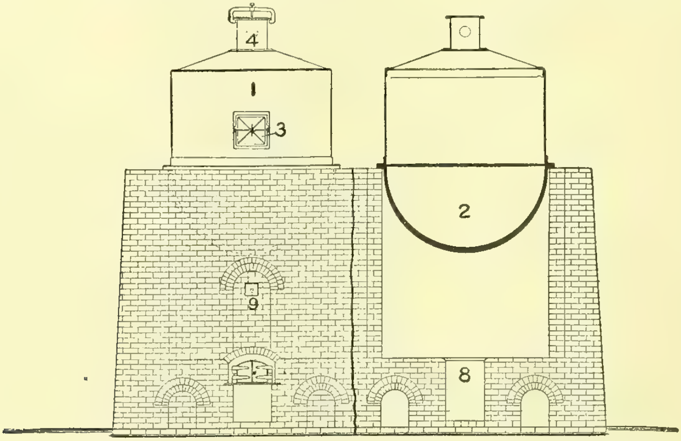

Fig. 7.—Elevation and Front Section of Still (2,000 gals. capacity).

the coking is twenty to twenty-four hours. After the still is coked steam is kept on for three or four hours, and the furnace-doors are thrown open. In eight to ten hours after coking the still doors are thrown off, and in forty-eight hours after firing the still is cleaned by cleaners, who pick the coke from the bottom, and the still is again ready for charging. Seven runs per fortnight are thus got from one still. This is the simplest form of distillation.

In some works a system of feeding the stills is carried on. As soon as the sp.gr. of the distillate has risen to ·820 or ·830, fresh oil is run in, and the distillation is started afresh. With 2,000-gallon stills this can be done, but with 2,500-gallon stills it is difficult to get seven runs per fortnight.

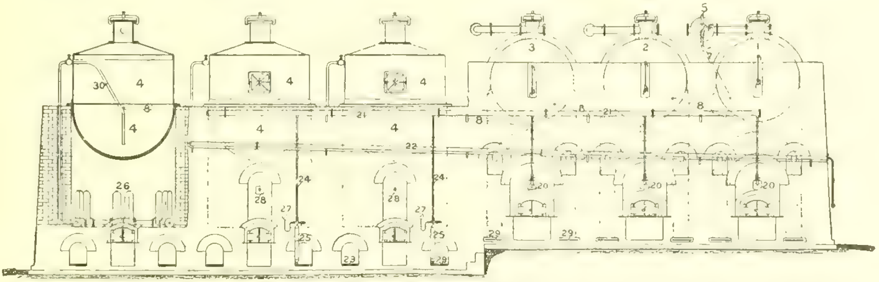

Fig. 8.—Continuous Distillation Plant (Front elevation with section of Still).

Description applicable to Figs. 8 and 9 :—1. No 1, or driving boiler. 2 No. 2, or medium boiler. 3. No. 3, or heavy oil boiler. 4. Coking stills. 5. Cold oil feed to heater. 6. Heater. 7. Hot oil feed from heater to boiler. 8. Transfer pipes between boilers and stills. 9. Condenser. 10. Incondensible gas exhaust. 11. Worm end, or trap pipe. 12. Oil receiving pipes. 13. Worm end platform. 14. Safety plug. 15. Gauge glass and cocks. 16. Furnace 17. Ports for heated gases 18. Arch. 19. Arch protecting transfer pipe. 20. Tar blower or injector. 21. Steam main. 22. Tar main. 23. Boiler steam connection 24. Still steam connection. 25. Water trap. 26. Steam superheater. 27. Steam pressure gauge 28 Spy boxes. 29 Dampers. 30. Still steampipe.

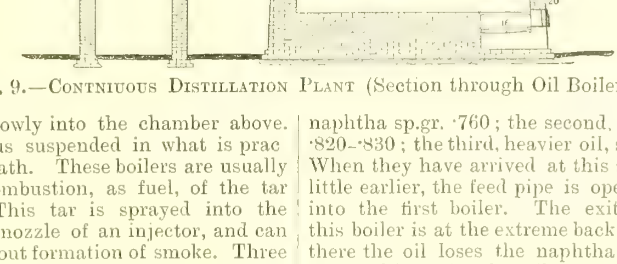

Fig. 9.—Contniuous Distillation Plant (Section through Oil Boiler).

Mr. Henderson, of Broxburn, recently introduced a process of continuous distillation, which, while effecting a large saving in coal and labour, enables much smaller plant to do the work. The system consists of a series of oil stills and boilers, kept at different temperatures, the colder oil is fed into the first, and, after passing through the series, is reduced to dryness in the last, of which there are always two or more. Before entering the first boiler the oil is led through a heater, and heated by the gases coming from the hottest of the boilers. These boilers are usually made for continuous distillation, of a size 19 feet long and 7 feet deep, and the bottom, at least, made of the best procurable iron or steel. In oil boilers the steam pipe is laid along the bottom, and the steam escapes by a series of perforations. Immediately below the boilers an arch is built the whole length of the furnace; this arch is perforated at the sides and back with port-holes, which allow the hot furnace gases to escape slowly into the chamber above. The boiler is thus suspended in what is practically a hot-air bath. These boilers are usually heated by the combustion, as fuel, of the tar from the oil. This tar is sprayed into the furnace from the nozzle of an injector, and can be consumed without formation of smoke. Three boilers, with the necessary stills for coking, form a complete set, though fewer can be done with, depending on the quantity of oil and the number of fractionations. The oil feed-pipe delivers its contents within 18 inches from the front of the first boiler. At first all the boilers are filled with cold oil, and are gradually worked to their normal state, viz. the first boiler distilling naphtha sp.gr. ·760; the second, light oils, sp.gr. ·820-·830; the third, heavier oil, sp.gr. ·870-·880. When they have arrived at this stage, or even a little earlier, the feed pipe is opened and oil fed into the first boiler. The exit oil pipe from this boiler is at the extreme back, and in passing there the oil loses the naphtha or lighter oils. From this exit the oil flows by gravitation through pipes to the front of the next boiler, in passing through which it loses light oils sp.gr. ·820-·830, and in the same manner into the next, where in its passage it loses most of the heavier oils and solid paraffin. It will thus be seen that the heavy dirty residue all accumulates in the third boiler. When the boiling-point of this residue rises so that the heat required to distil it might deposit coke, although in actual practice it is never allowed to go so far, the cock is opened between the third boiler and one of the attached stills with a cast-iron bottom, previously heated to the distilling-point, and filled with an atmosphere of steam. The operation requires great care, for if the still be too cold the oil froths up, and may burst the still by solidifying in the condenser. In practical working, when one still has had sufficient run into it, another is made ready, and there is no stoppage.

In the first distillation which the crude oil receives, naphtha sp.gr. ·740 only is separated, the rest of the distillates are run together and form what is known as *once-run oil.* In some works where the 'Young and Beilby' retorts are in use the crude distillation is omitted. After distillation the oil receives its first treatment with sulphuric acid and soda. This operation is conducted as a rule in large malleable iron boilers containing 6,000–15,000 gallons. These boilers are set on different levels so that the oil after purification with acid may run into the boiler, where it is to receive the soda treatment. Agitation is produced by means either of air at high pressure, applied through a perforated pipe lying at the bottom of the washer, or by ordinary mechanical means, such as paddles set on a shaft extending the whole length of the washer. The acid is added in successive portions, with an intervening settling and withdrawal of the tar.

The mixed distillates from the crude oil are treated at the lowest workable temperature—heat being necessary on account of the presence of solid paraffin—with either the acid tar from some of the later stages of the treatment or with acid sp.gr. 1·720 or 144°Tw. This treatment precipitates the greater part of the tarry matter of the oil consisting of pyridine bases, pyrrol, &c. In practice this operation is known to be complete when the oil changes from a bright-green colour to a very pronounced blue. After the acid treatment the oil is allowed to settle for not less than 4 hours, and more usually overnight. When the precipitated tar has completely settled out the oil is run into the soda washer, where it is treated either with soda from a later stage or with 1½–2 p.c. solution caustic soda sp.gr. 1·3 (60°Tw.). This soda absorbs the cresylic and phenylic bodies. The complete absorption of these bodies is known when a little clear soda liquor appears at the pipe for drawing off the soda tar.

The oil after this treatment is ready for fractional distillation into heavy and light oil. This is done in boilers or stills similar to those described, and may be either intermittent or continuous. The distillate is run into the light-oil-receiving tank so long as the sp.gr. is below ·830–·840; after it has reached that sp.gr. it becomes solid on cooling, and therefore requires to be sent to the paraffin extraction house in order that the solid paraffin may be separated.

The first fraction contains nearly all of the burning or paraffin oil of commerce. It is washed with acid, usually about 0·5–0·75 p.c., and after agitation, settling, and withdrawal of the tar, which is again used for treating the *once-run oil*, it is treated with caustic soda solution sp.gr. 1·3 (60°Tw.), usually about 1–1·25 p.c., and again distilled. In this distillation boilers are in more general use, and the residues are either drawn off, as in the continuous distillation, or the boilers are, after repeated feeding operations, allowed to cool and the residue drawn off into cast-iron coking stills. Any portion of the distillate over ·840 is run to the paraffin extraction house.

When the light oil has reached this stage it can, by a single washing, be made ready for the market; but the largest proportion of oil made receives another washing with strong acid and strong caustic soda and another distillation, all similar to that which it received before. The oil in this state can be pumped to the stock tanks as finished. If, however, a better quality of oil be wanted, paler in colour and with less smell, it has to undergo a washing differing slightly from those which have been described. As before, the oil is washed with strong acid, but in one treatment, and allowed to settle for 15 minutes. The tar is then withdrawn and the oil is run into the soda washer and treated first with either pure water or with 10 p.c. soda solution sp.gr. 1·0025 (½°Tw.). This is allowed to settle out and withdrawn, and 8–10 p.c. soda solution sp.gr. 1·015 (3°Tw.) run in, and the oil agitated with it for 5 or 10 minutes. This is allowed to settle out, and thereafter the oil receives two washings with pure water to wash out the remaining traces of soda. It is then taken to some shallow vessels, kept in a temperature of say 15·5°–21°C., when the water rapidly separates out and the oil is white, bright and clear, with little smell.

Heavy oil and paraffin fraction.—From this fraction the greater proportion of the paraffin is immediately extracted. The oil is cooled as slowly as possible to the temperature desired so that the crystals may be large and well formed. In some processes the whole of the paraffin is extracted at this stage by cooling the oil to a very low temperature, but in the majority of cases only 80–90 p.c. of the paraffin is extracted. The plant employed in the cooling operation varies greatly. The oldest system yet in use is that in which the oil, placed in a shallow vessel, constantly fed, is lifted on the surface of a slowly revolving drum fixed so that a small part of its circumference moves in the oil; the drum is kept at a very low temperature by means of either the expansion of gasoline or ether within it or by the circulation of frozen brine cooled by any of the freezing machines in general use. At the opposite side from which the drum emerges from the oil is fixed a knife-edge, regulated in its distance from the surface of the drum by screws, which, scraping the oil frozen in transit, throws it down to a pump, which conveys it to filter presses. It is found that this system of cooling is much too rapid, and that the crystals are not well formed. Various attempts have been made to rectify this, among the more successful of which have been the apparatus of Henderson and of Beilby. In both of these systems the oil is cooled in bulk. In the Henderson system a large vessel, in which are suspended hollow plates with brine circulating through them, is filled with oil and slowly frozen. The oil as it freezes is removed from the cold surface of the hollow plates by slowly revolving scrapers, and a screw at the bottom delivers it, when cooled to a sufficiently low temperature, to the pumps. These vessels are covered with wood to prevent radiation.

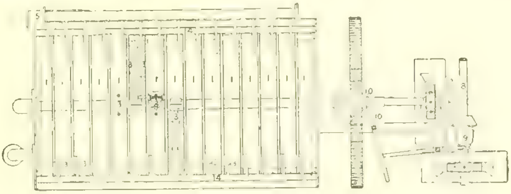

Fig. 10.—Henderson's Patent Paraffin Cooler (Plan).

Description applicable to Figs. 10, 11, and 12:—1. Oil space or cells. 2. Oil overflow pipe. 3. Scrapers for solidified paraffin. 4. Screw propellers. 5. Exit valve for frozen oil to pumps. 6. Scraper shaft. 7. Screw shaft and driver for scraper shaft. 8. Main driving shaft. 9. Disengaging gear for cooler. 10. Disengaging gear for scraper shaft. 11. Cold brine inlet to brine cells. 12. Brine cells. 13. Brine outlet from cells to shell space. 14. Brine space round shell. 15. Brine overflow.

In the Beilby system the oil is cooled in repose to a solid mass in large blocks; when the block is frozen through, a shearing screw at the bottom breaks it up and conveys it to the pumps. Beilby also builds both cooling and filtering apparatus in a house built with double walls and roof, the interspaces being filled with non-conducting material. The oil is thus filtered at practically the same temperature as that to which it has been cooled.

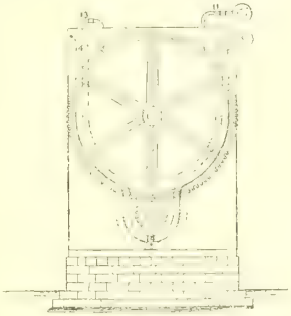

Fig. 11.—Henderson's Patent Paraffin Cooler (End elevation).

The oil, after being frozen by any of the foregoing systems, is pumped into an ordinary filter-press, which retains the paraffin crystals and allows the oil to run off. These filter-presses are, as a rule, allowed to attain a maximum pressure of 160 lbs. per square inch.

The oil from which the paraffin has been extracted is now washed with 1–1·7 p.c. sulphuric acid, 1·840 sp.gr., as before described, and after settling and withdrawal of the tar, it is treated with 1–1¼ p.c. caustic soda solution sp.gr. 1·3 (60° Tw.). After this treatment it is technically known as blue oil, and is again distilled in large cast-iron stills. This oil is always distilled over soda, about 5 lbs. per 100 gallons being put into the still. A very good plan is to hang 1 cwt. drums solid caustic soda from the top of the still. In this way the soda is slowly dissolved out and the whole of the oil receives a due share, whereas when the soda is thrown into the still, it settles to the bottom of the oil and the coke which is formed covers it over and thus neutralises the full benefit. In this distillation the oil is fractionated: until it reaches a sp.gr. of ·840–·845 it is returned to the light oil, from ·840–·845 to ·865–·875 it is fractioned to form light mineral lubricating oil, and from ·865–·875 until the oil in the still begins to undergo destructive distillation the distillate forms heavy mineral lubricating oil. These oils still contain solid paraffin, and are again frozen in order to extract it. After being filtered, the oils are washed, the heavier with from 3–5 p.c. 1·840 sp.gr. sulphuric acid, the lighter with from 2–3 p.c. added from time to time, with intervening agitation, settling, and withdrawal of the tar. After the last addition they are usually allowed to settle overnight. Having been thoroughly settled, they are

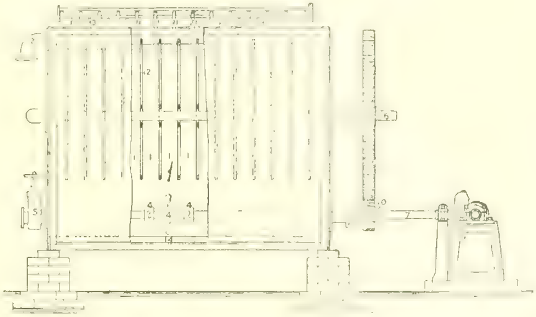

Fig. 12.—Henderson's Patent Paraffin Cooler (Side elevation with break to show arrangement of Plates and Screw).

run into the soda washer and treated with warm carbonate of soda solution sp.gr. 1·045 (9°Tw.), or with sp.gr. 1·020 (4°Tw.) sol. caustic soda. When the acid has been completely neutralised a large quantity of warm water (70°C.) is run in and the oil is allowed to settle. After settling for some time, the soda solution—which now mainly consists of an emulsion of soda solution and sodium-sulpho-olefines, the olefines having been attacked in the previous acid treatment in the endeavour to remove all the impurities from the oil—is run off and more warm water added. After this has partially settled out and withdrawn, the oil is kept at a temperature of from 100–150°F. for some hours in shallow open vessels when the remainder of the water settles out and the oil is clear. The heavier oil has usually a sp.gr. ·885–·895 and is largely used for lubricating light machinery. The lighter oil is used for gas-making and for cleaning machinery.

The paraffin from the filtering of all these oils, the blue oil, the heavy lubricating oil, and the medium or light mineral oil, still contains a large percentage of oil varying from 15–30 p.c., and this oil requires to be extracted by hydraulic pressure. The paraffin as it comes from the filter-presses is made up in cakes surrounded by cotton press cloth, and when in the press a piece of wicker basket-work is placed below each cake to allow the oil to drain freely. The hydraulic presses are kept at a constant temperature by means of steam-pipes placed in close proximity. After pressure, the 'scale,' as it is called, from the blue oil varies from green to light grey in colour, has a melting-point of 45·5°–49°C., varying as the oil it has been extracted from was cooled before filtering—the lower temperature yielding the lower melting-point scale, and it seldom contains less than 4 p.c. oil and 2 p.c. dirt and water and other impurities. It is known commercially as green or hard scale.

The 'scale' from the heavy and light mineral lubricating oils is much lower in melting-point, varying from 28·3°–38·8°C., and is known commercially as soft scale. This soft scale when remelted is used very largely for the dipping of matches, and has thus very generally acquired the name of match paraffin.

The hard scale m.p. 45·5°–49°C. is, after refining, used in the manufacture of candles. At present there are two very distinct processes for refining this scale and converting it into wax suitable for candle manufacture. These are known respectively as the 'naphtha' and the 'sweating' process. The first, which is the older, has now been almost replaced by the latter, mainly on account of economy and safety.

In the 'naphtha' process the hard scale alone is taken. It is melted in a suitable vessel and the dirt and water allowed to settle. Naphtha, either pure or from a later stage, is added to the extent of 10–20 p.c., and the whole mass is allowed to cool slowly. The cooling may be done by floating the melted paraffin on the surface of water in a shallow pan to a depth of $1\frac{1}{2}$–2 inches, or in pans suitable for the purpose. The mixed paraffin and naphtha is pressed by hydraulic power, the presses being usually inclosed in a casing heated with steam-pipes. The naphtha carries off the lower-melting-point paraffins, oil, and greasy hydrocarbons, and leaves the paraffin much whiter than before pressing. This operation is repeated three or four times until a sufficient degree of purity is attained, the naphtha from each stage being used for admixture with the paraffin of the previous stage. The purified paraffin still smells strongly of spirit, from which it is freed by heating with open steam in a closed vessel connected with a condenser, when the naphtha distils over and leaves the paraffin odourless. It is then thoroughly settled and freed from water, treated with 2–5 p.c. animal charcoal and filtered through steam-jacketed filters. The resulting paraffin from this process is beautifully white, bright, and translucent. The melting-point of the wax is thoroughly within control. The naphtha pressings from the first treatment containing all, or nearly all, of the total impurity are freed from naphtha by open steam distillation, the distilled naphtha being used again in the last stage of the refining process. The residue in the still is treated with sulphuric acid and soda, as in treating finished oil, and after settling, cooling, and pressing to remove oil, is soft or match paraffin.

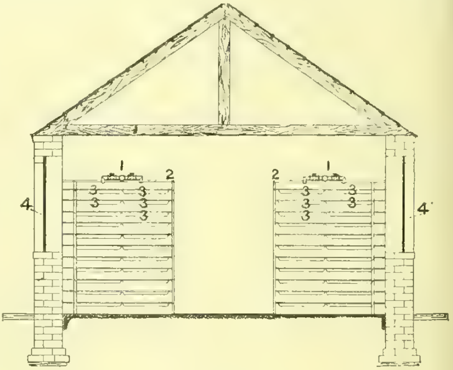

Fig. 13.—Paraffin Cooling House.

1. Paraffin pipes. 2. Cooling rack. 3. Cooling trays. 4. Windows.

When, on the other hand, paraffin is to be purified by the 'sweating process' the whole of the paraffin from the oils is taken, both hard and soft, so that the paraffin to be dealt with may contain a considerable proportion of paraffin of a lower melting-point than the finished wax is to have. It is melted and cooled slowly in tins placed one above another and so arranged that when the upper tin is full the liquid paraffin overflows into the next below. A cake 2 feet long by 1 foot broad by $1\frac{1}{2}$–2 inches thick should take twelve hours to cool, so that the crystals may be well developed. These cakes are then transferred into either large heated ovens, or into smaller compartments inclosed in a suitable building. Fig. 14 exhibits one of the larger ovens in section. On each side and at the bottom are steam-pipes, and half way up are plates to deflect the heat. Next come two racks, fitted with inclined shelves, perforated at the edges so that the drainings may escape freely. The cakes of paraffin are

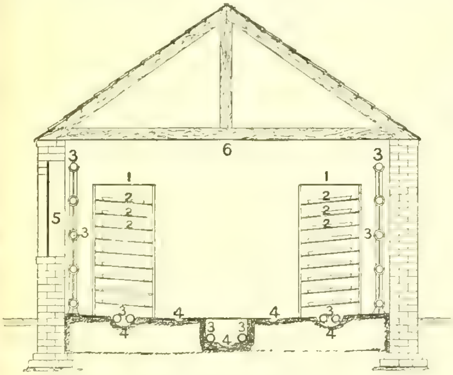

Fig. 14.—Paraffin Sweating House.

1. Sweating racks. 2. Paraffin cakes. 3. Steam heating pipes. 4. Oil sweatings gutter. 5. Window. 6. Close roof.

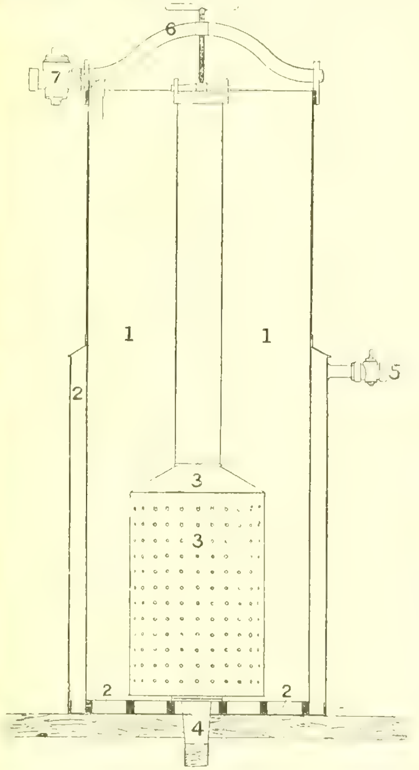

Fig. 15.—Paraffin Filter (Steam-jacketed).

1. Paraffin receiver. 2. Steam jacket. 3. Filter cone covered with gauze and paper. 4. Filtered paraffin exit. 5. Steam cock. 6 Bridge and screw for keeping filter in position. 7. Unfiltered paraffin cock.

laid upon these shelves with an intervening sheet of cocoa matting or other suitable material allowing of free drainage. Steam is then turned on to the heating pipes, all openings into the building closed, and the oven is heated to within $2\frac{1}{4}$–$3\frac{1}{3}$°C. of the desired melting-point of the finished paraffin. As the heat rises, the lower-melting-point paraffin crystals melt, and carry away with them the oil and impurity, and after a lapse of 10–12 hours the hard paraffin is left almost perfectly pure. It is then melted, treated with animal charcoal, filtered and caked. If a purer paraffin be desired, the cakes from the oven are mixed with some white, lower-melting-point paraffin, and the operation of sweating again gone through, the sweating from the second operation being added to the crude paraffin of the first.

The sweatings from the crude paraffin are caked, pressed by hydraulic power to free them from oil, and are again themselves sweated to make a lower-melting-point wax. A very good plan, where the cooling power is ample, is to mix the sweatings with the light lubricating mineral oil before freezing for the last time. The oil removes the dark-coloured impurities, and the scale is fit either for melting into match paraffin, or for mixing with the crude green scale previous to sweating. The usual plan, however, is to treat the second sweatings with sulphuric acid and soda, as in treating a finished oil, and cake for match paraffin.

Besides these, the usual commercial products of paraffin manufacture, there are certain products obtained from the acid and soda tars. Generally, the acid tar is boiled with water, which separates the acid from the greater part of the alkaloidal bases precipitated by it, and the resultant weak acid liquor is used in the manufacture of sulphate of ammonia. In most works, except where the yield of ammonia per ton is exceptionally large, the acid recovered in this way is sufficient to convert the whole of the ammoniacal compounds obtained from the shale into sulphate. The acid and soda tars are then mixed together and either used as fuel, or distilled to make oils for gas-making and coarse greases for lubricating colliery hutches.

A process is still in use for recovering the soda after its absorption of cresylic and phenylic tars. Carbonic acid from a coke fire is forced through the soda tar as it comes from the washers. The acid combines with the soda, and creosote oil is liberated suitable for creosoting sleepers, and for other purposes. The sodium carbonate is reconverted into caustic and used over again.

Statistics.

British manufacture, 1890.

Retorts in Operation.

Henderson's patent . . .	1,520
Young and Beilby's patent .	3,528

Capable of producing:
64,560,000 gallons crude oil and
25,000 tons sulphate of ammonia per annum.

This crude oil yields:

Naphtha . . .	2,030,128	gallons
Burning oil . . .	19,086,656	,,
Gas oil 840-50 . .	973,768	,,
Medium oil ·865 . .	2,729,928	,,
Heavy lub. oil ·875–·895 .	6,440,632	,,
Soft scale . . .	3,605	tons
Hard scale . . .	17,482	,,

J. C. H

PARAGUAY TEA. This substance, commonly known as *Maté*, or Jesuits' or St. Bartholomew's tea, consists of the dried leaves and shoots of an evergreen, *Ilex paraguayensis*, and other small trees of the same genus, common in the mountain woods of Southern Brazil, the Argentine Republic, and Paraguay. The dried leaf is used as a substitute for tea in these countries. Its properties appear to be chiefly due to caffeine, which is present, according to Stenhouse, to the extent of from 1·1 to 1·2 per cent.

A sample of the powdered leaves examined by H. Byasson (Ph. [3] 8, 605) gave the following results:

Caffeine	1·85
Glutinous substances &c.	3·87
Complex glucoside	2·38
Resin	0·63
Inorganic salts, including iron	3·92
Malic acid	Not estimated.

According to Alonzo Robbins, it contains 1·5 of a peculiar tannin which does not precipitate potassio-tartrate of antimony, nor tan leather.

PARAPHENYLENE BLUE. This dye comes into commerce in three shades, which are designated respectively G, R, and B. They belong to a class of dyes obtained (according to Eng. Pat. 10,134, 1886) by heating paraphenylenediamine (or its homologues) with certain amidoazo- compounds—*e.g.* amidoazobenzene.

Paraphenylene blue R dissolves easily in water with a reddish-blue colour. Hydrochloric acid produces no change in the aqueous solution; but caustic soda completely precipitates the dye in the form of a dark-violet precipitate. Tannic acid, in presence of sodium acetate, yields a blue precipitate, and the liquid is rendered colourless. The boiling aqueous solution yields a black precipitate with bichromate of potash. The reactions shown by the other shades are similar. On wool, paraphenylene blue dyes direct in presence of a small quantity of acid. On cotton it is fixed by means of tannin and tartar emetic. The shades obtained resemble those produced by methylene blue. When chromed after dyeing the shades become considerably darker (S. C. I. 7, 561).

PARALDEHYDE *v.* ALDEHYDE.

PARASACCHARIC ACID *v.* LIQUORICE ROOT.

PARAXANTHINE *v.* VEGETO-ALKALOIDS.

PARCHMENT. *Parchemin* (Fr.); *Pergament* (Ger.). This writing material has been known since the earliest times, but is now made in a very superior manner to that by which it was anciently prepared, as we may judge by inspection of the old vellum and parchment manuscripts. The art of making parchment consists in certain manipulations necessary to prepare the skins of animals of such thinness, flexibility, and firmness as may be required for the different uses to which this substance is applied. Though the skins of all animals may be converted into writing materials, only those of the sheep or the she-goat are used for parchment; those of calves, kids, and dead-born lambs for vellum; those of the he-goat, she-goat, and wolves for drum-heads; and those of the ass for battledores. All these skins are prepared in the same way, with slight variations, which need no particular detail.

They are first of all prepared by the leather-dresser. After they are taken out of the lime-pit, shaved, and well washed, they must be set to dry in such a way as to prevent their puckering and to render them easily worked. The small manufacturers make use of hoops for this purpose, but on the larger scale a *herse* or stout wooden frame is employed. This is formed of two uprights and two cross-bars solidly joined together by tenons and mortices so as to form a strong piece of carpentry, which is to be fixed against a wall. These four bars are perforated all over with a series of holes of such dimensions as to receive slightly-tapered boxwood pins truly turned, or even iron bolts. Each of these pins is transpierced with a hole like the pin of a violin, by means of which the strings employed in stretching the skin may be tightened. Above the *herse* a shelf is placed for receiving the tools which the workman needs to have always at hand. In order to stretch the skin upon the frame, larger or smaller skewers are employed, according as a greater or smaller piece of it is to be laid hold of. Six holes are made in a straight line to receive the larger, and four to receive the smaller skewers or pins. These small slits are made with a tool like a carpenter's chisel, and of the exact size to admit the skewer. The string round the skewer is affixed to one of the bolts in the frame, which are turned round by means of a key like that by which pianos and harps are tuned. The skewer is threaded through the skin in a state of tension.

Everything being thus prepared, and the skin being well softened, the workman stretches it powerfully by means of the skewers; he attaches the cords to the skewers, and fixes their ends to the iron pegs or pins. He then stretches the skin, first with his hand applied to the pins, and afterwards with the key. Great care must be taken that no wrinkles are formed. The skin is usually stretched more in length than in breadth, from the custom of the trade, though extension in breadth would be preferable, in order to reduce the thickness of the part opposite the backbone.

The workman now resorts to the fleshing tool. It is a semicircular, double-edged knife, made fast in a double wooden handle. Other forms of the fleshing-knife edge are also used. They are sharpened by a steel. The workman seizes the tool in his two hands so as to place the edge perpendicularly to the skin, and, pressing it carefully from above downwards, removes the fleshy excrescences and lays them aside for making glue. He now turns round the *herse* upon the wall, in order to get access to the outside of the skin and to scrape it with the tool inverted, so as to run no risk of cutting the epidermis. He thus removes any adhering filth, and squeezes out some water. The skin must next be ground. For this purpose it is sprinkled upon the fleshy side with sifted chalk or slaked lime, and then rubbed in all directions with a piece of pumice-stone, 4 or 5 inches in area, previously flattened upon a sandstone. The lime soon gets moist from the water contained in the skin. The pumice-stone is then rubbed over the other side of the skin, but without chalk or lime. This operation is necessary only for the best parchment or vellum. The skin is now allowed to dry upon the frame, being carefully protected from sunshine and from frost. In the arid weather of summer a moist cloth needs to be applied to it from time to time, to prevent its drying too suddenly, immediately after which the skewers require to be tightened.

When it is perfectly dry, the white colour is to be removed by rubbing it with the woolly side of a lambskin. But great care must be taken not to fray the surface—a circumstance of which some manufacturers are so much afraid as not to use either chalk or lime in the polishing. Should any grease be detected upon it, it must be removed by steeping it in a lime-pit for ten days, then stretching it anew upon the *herse*, after which it is transferred to the *scraper*.

This workman employs here an edge tool of the same shape as the fleshing-knife, but larger and sharper. He mounts the skin upon a frame like the *herse* above described; but he extends it merely with cords, without skewers or pins, and supports it generally upon a piece of raw calfskin strongly stretched. The tail of the skin being placed towards the bottom of the frame, the workman first pares off with a sharp knife any considerable roughnesses, and then scrapes the outside surface obliquely downwards with the proper tools till it becomes perfectly smooth; the fleshy side needs no such operation; and indeed, were both sides scraped, the skin would be apt to become too thin, the only object of the scraper being to equalise its thickness. Whatever irregularities remain may be removed with a piece of the finest pumice-stone well flattened beforehand upon a fine sandstone. This process is performed by laying the rough parchment upon an oblong plank of wood in the form of a stool, the plank being covered with a piece of soft parchment stuffed with wool, to form an elastic cushion for the grinding operation. It is merely the outside surface that requires to be pumiced. The celebrated Strasburg vellum is prepared with remarkably fine pumice-stone. If any small holes happen to be made in the parchment they must be neatly patched by cutting their edges thin and pasting on small pieces with gum-water.

Parchment is coloured green only. The following is the process. In 500 parts of rain-water boil 8 of cream-of-tartar and 30 of crystallised verdigris; when this solution is cold, pour into it 4 parts of nitric acid. Moisten the parchment with a brush, and then apply the above liquid evenly over its surface. Lastly, the necessary lustre may be given with white-of-eggs or mucilage of gum arabic (Ure).

PARCHMENT PAPER *v.* Cellulose.

PARICINE *v.* Vegeto-alkaloids.

PARIGENIN and **PARIGLIN** *v.* Sarsaparilla.

PARILLIN *v.* Glucosides; also Sarsaparilla.

PARILLINIC ACID *v.* Sarsaparilla.

PARIS BLUE. This term is occasionally applied to Prussian blue, and also to the products obtained by heating aniline with stannic chloride.

PARIS LAKE. *Carmine lake v.* Lakes.

PARIS RED. A variety of rouge employed for polishing.

PARIS YELLOW. *Normal lead chromate v.* Chromium.

PARTING. The separation of gold and silver by means of nitric acid, *v.* Assaying.

PASTES *v.* Gems, artificial.

PASTE YELLOW *v.* Azo- colouring matters.

PATCHOULI. *Patchupat* or *Patschapat.* The herb *Pogostemon patchouli* of the family *Labiatæ*, a shrubby plant about two feet high, a native of Sylhet, Penang, and Malacca. It affords the celebrated patchouli perfume of the Hindus. The odoriferous parts of the plant are the leaves and young tops which by distillation yield a volatile oil from which essence of patchouli is prepared. The coarsely powdered leaves are used to perfume sachets &c. The odour is peculiar, and, to some people, disagreeable; but it is much esteemed by many both in India and Europe. Ill effects, such as loss of appetite and sleeplessness, have been ascribed to the excessive use of the perfume.

The odour of the patchouli plant is due to an essential oil which is obtained by distillation. This oil is of great density, and when dissolved in alcohol in the proportion of two ounces of oil to one gallon of alcohol forms the commercial essence of patchouli. The oil is one of the least volatile of any known essential oils, and its odour is consequently one of the most permanent. It will not congeal, except at exceedingly low temperatures, unless extracted from plants which have been gathered several years, when more than half the product will assume a crystalline form, whilst the perfume from it is far less powerful.

When the essential oil is submitted to fractional distillation, a peculiar blue body is formed at the highest temperature, which was named by Piesse *azulene*.

The camphor or stearoptene obtained from the essential oil is purified by solution in alcohol and then in ether, from which it crystallises in hexagonal prisms. It melts at 55°-56°C., boils at 206°, and has a vapour-density of 8·00. Heated with zinc chloride, it loses water, and leaves a hydro-carbon $C_{15}H_{24}$ or $C_{15}H_{26}$ (?).

PATCHOULI CAMPHOR *v.* Camphors.

PATENT FUEL *v.* Fuel; also Pitch.

PATENT LEATHER VARNISH *v.* Varnish.

PATERAITE *v.* Molybdenum.

PATINA. The green film which forms upon bronze and copper mouldings, and consisting of basic copper carbonate. On bronze statues it produces a pleasing effect owing to its colour, smoothness, and transparency, so that the bronze itself may be seen through it in places. The conditions which favour the formation of patina are a pure atmosphere, the presence of moisture in the air or in the earth where the articles may have lain buried, and a smooth surface. The finest examples of patina are found upon bronzes of ancient manufacture in which much tin and little zinc was used as alloy. The effect of a natural, and consequently slowly formed, coating of patina is frequently imitated artificially by wetting articles of bronze with dilute acids.

PATRINITE. *Bismuth sulphide v.* Bismuth.

PAULLINITANNIC ACID *v.* Guarana.

PAVIIN *v.* Horse chestnut.

PAYTINE *v.* Vegeto-alkaloids.

PEACH WOOD *v.* Brazil wood.

PEACOCK-COPPER ORE. An iridescent copper pyrites produced by partial decomposition of the yellow ore $Cu_2S.Fe_2S_3$.

PEA IRON ORE *v.* Iron.

PEARLS. Calcareous concretions formed by various molluscs, those used in jewellery being mostly obtained from the large pearl oyster, *Avicula* (*Meleagrina*) *margaritifera*, or from the smaller *M. fucata*. The analysis of several fine white pearls by Dr. G. Harley gave calcium carbonate, 91·72; organic matter, 5·94; water, 2·23 (Pr. 43, 1888, 461). Most pearls present a concentric structure, having been formed by successive deposits around a nucleus, which may be a grain of sand, a parasitic organism, a fragment of seaweed, or some other foreign body which by irritating the mollusc stimulates the secretion of nacre. The pearls are usually found in the mantle, but sometimes in the muscles of the mollusc; or, having escaped from the tissues, they may become adherent to the shell. To be valued by the jeweller, the pearl should be of spherical form, while its skin or outer coat should display the delicate iridescent sheen known as the 'orient.' Pearls of more or less hemispherical shape, cut from the shell, are termed *boutons*; while those which are warty or irregular in form pass under the name of *baroque*. Occasionally the pearl is found completely embedded in the mother-of-pearl. Some pearls, instead of showing a concentric structure, are crystalline, being composed of striated prisms radiating from the centre, and these may or may not possess a nucleus (Harley, Pr. 45, 1889, 612).

The principal pearl fisheries are those of Torres Straits and North-Western Australia, the Sooloo Archipelago, Ceylon, and the coast of Madras, the Persian Gulf, and the Gambier and Pomotou Islands. The American fisheries are chiefly in the Caribbean Sea, off the coast of California, and near Panama. The pearls are mostly derived from *Meleagrina Californica* (W. H. Dall, Americ. Nat. 17, 1883, 579, 731; E. W. Streeter, Pearls and Pearling Life, London, 1886).

Coloured pearls are occasionally found, the tint in each case being dependent on that of the nacre lining the shell. The highly-prized black pearls are obtained chiefly from Mexico, and it has been suggested that the colour is due to the presence in the water of salts of silver, derived from neighbouring silver mines. Pearls have been artificially stained by means of silver salts. Pink pearls, sometimes finely water-lined, are mostly derived from the conch shell *Strombus gigas*; while large, coarse, yellowish pearls are obtained from the great clam, *Tridacna gigas*.

The principal source of fresh-water pearls is the pearl-mussel (*Unio margaritifera*), a mollusc widely distributed in the rivers of northern temperate regions. It is found in the Tay, Forth, Earn, Doon, and many other mountain streams in Scotland. Scottish pearl-fishing was revived in 1860, and successfully carried on for some years by M. Unger. The pearl-mussel is also found in Cumberland; in Wales, especially in the Conway; and in Ireland. On the Continent pearl-fishing has been prosecuted in Saxony, Bohemia, and Bavaria; and in Norway, Sweden, and even Lapland. The American rivers also yield pearl-bearing molluscs, especially in New England, New Jersey, and Ohio; and in Canada (G. F. Kunz, Gems of N. America, New York, 1890). Fresh-water pearls are likewise obtained from China and Japan, and the Chinese exhibit much skill in inducing the formation of pearl by the artificial introduction of certain objects, upon which the mollusc deposits a nacreous layer. Chinese shells with images of Buddha formed of pearl adherent to the inner surface are well known to collectors (Macgowan, Journ. Soc. Arts, 2, 1853, 72).

The so-called cocoa-nut pearls, from the Malay Archipelago, are pearl-like bodies, resembling ivory, said to be found inside cocoanuts. Certain bodies which have been described as mammalian pearls are simply biliary concretions, formed mainly of cholesterin.

Artificial pearls are manufactured on the Continent in a variety of ways. Some are globes of thin opaline glass, filled with gum or wax, and deadened on the surface by means of hydrofluoric acid. The better kinds are glass globules lined with a nacreous composition, formed by digesting the silvery scales of the bleak in ammonia. Roman pearls are glass spheres, to which the nacreous material is applied externally. Celluloid, incorporated with fish scales, has become a favourite material for artificial pearls. Black pearls have been imitated by beads of a very compact hæmatite, which may be polished so as to present a kind of plumbago-lustre. Pink pearls are frequently confounded with beads of pale coral (*v.* MOTHER-OF-PEARL). F. W. R.

PEARL ASH. A variety of potassium carbonate, *v.* POTASSIUM.

PEARL SINTER. A kind of opal found in the cavities of volcanic tufa.

PEARL SPAR *v.* DOLOMITE.

PEARL STONE. A felspathic mineral with a pearly lustre occurring in spheroidal concretions.

PEARL WHITE is (1) a basic bismuth nitrate or oxychloride (*v.* BISMUTH); (2) a preparation of mother-of-pearl.

PEAT and **TURF** *v.* FUEL.

PELARGONIC ACID *v.* FATTY ACIDS.

PELLETIERINE *v.* VEGETO-ALKALOIDS.

PELLITORY RESIN *v.* RESINS.

PENNETTIER'S GREEN. *Hydrated chromium sesquioxide v.* CHROMIUM.

PENTADECATOIC ACIDS *v.* FATTY ACIDS.

PENTOIC or **VALERIC ACIDS** *v.* FATTY ACIDS.

PEPPER. The pepper of commerce is the dried fruit of *Piper nigrum*, cultivated in the East and West Indies, Java, Sumatra, &c. The pepper vine under cultivation is kept at a height of about 12 feet, although it reaches 20 feet or more if left to grow. Its fruit appears after three years, and the plant remains productive for seven or eight years more. The berries or drupes are gathered before they are fully ripe and spread out to dry, whereupon they become black and shrivelled instead of red as before. This is black pepper. White pepper is the same fruit decorticated, its whiteness being sometimes increased by bleaching with chlorine. In regard to value, the heavier the sample of pepper the more it is esteemed by the merchant.

Examined under the microscope, a section of peppercorn exhibits six layers of distinct character—namely (1) a layer of large elongated cells; (2) a layer of small angular cells; (3) a layer of woody fibre and spiral vessels; (4) a layer of large round cells; (5) a layer of coloured cells; (6) a layer of colourless cells. In its ground state, the cellular structure varies somewhat in different kinds, and the recognition of its forms is a matter requiring considerable experience. For the most part the cells have sharp acute angles, and the starch granules are very small and quite round.

Black pepper is stimulant, carminative, and rubefacient. It is useful in moderation as a condiment to persons who suffer from weak digestion; but in inflammatory habits or in affections of the mucous membrane it is generally highly injurious. As a medicine it is often serviceable in nausea, vomiting, chronic diarrhœa, and agues.

The following table, taking into account the amount of moisture, piperine, resinous extract, and ash, shows the result of six samples of pure pepper from various sources, and of long pepper (*Chavica officinarum*):—

—	Hygroscopic moisture	Piperin in pepper dried at 100°	Resin in pepper dried at 100°	Aqueous extract in pepper dried at 100°	Ash in pepper dried at 100°	
					Soluble in water	Total
	p.c.	p.c.	p.c.	p.c.		
Penang	9·53	5·57	2·08	18·33	2·21	4·18
Tellicherry	12·90	4·675	1·70	16·5	3·38	5·77
Sumatra	10·10	4·702	1·74	17·59	2·62	4·31
Malabar	10·54	4·632	1·74	20·37	3·45	5·19
Trang	11·66	4·600	1·70	18·17	2·53	4·77
White pepper (commercial)	10·30	5·600	2·05	—	0·56	1·12
Long pepper	—	1·800	0·80	16·82	4·47	8·30

A sample of Penang pepper, analysed by A. Wynter Blyth, showed the following composition:

General Composition of Pepper.

Volatile oil	1·04
Acrid resin	1·77
Piperin	5·17
Substances soluble in water, gum, starch, and other matters, subtracting ash	14·74
Substances insoluble in alcohol and in water	67·75
Water	9·53
	100·00

The ash of Tellicherry pepper gave:

Potash	24·380
Soda	3·226
Magnesia	13·000
Lime	11·600
Iron	0·300
Phosphoric acid	8·470
Sulphuric acid	9·613
Chlorine	7·570
Carbonic acid	14·000
Sand	6·530

Pepper contains an alkaloid (*piperine*); a brown alkaline fluid (*piperidine*); a volatile oil; and gum, starch, vegetable albumen, salts, and other substances.

Pepper is frequently adulterated. The adulterants detected are flour and sago starches, linseed meal, rice, potato, capsicum, olive stones, pepper refuse, the fruit of *Chavica officinarum* and *C. Roxburghii* or long pepper, sand, &c. The detection of adulteration is for the most part effected by means of the microscope; the quantitative determination is not easy because the relative amounts of the constituents of genuine pepper vary. Thus the quantity of piperine extends within rather wide limits, as also does the quantity of starch. Adulteration by the addition of ground olive stones and pepper refuse is the subject of a paper by H. Rabourdin (J. Ph. [5] 9, 289). The character of the adulterant being detected by the microscope, the pepper is boiled with its own weight of sulphuric acid and 100 times its weight of water. The presence of olive stone is shown by the reddish powder which settles to the bottom of the flask on standing (A. Wynter Blyth, Foods, their Composition and Analysis; Chevallier, Ann. d'Hygiène; Cooley's Dict. of Practical Receipts; An. vol. 13, 81–87).

Cayenne pepper is the powdered pods of *Capsicum annuum*, nat. ord. *Solanaceæ*. It possesses a very strong acrid principle, which is still more developed on heating the particles. The following analysis by Stromer shows the general constitution of cayenne pepper:

—	Seeds	Capsules	Whole fruit
Water at 100°C	8·12	14·75	11·94
Nitrogenous matter (protein)	18·31	10·69	13·88
Fat (ether extract)	28·54	5·48	15·26
Non-nitrogenous extractives	24·33	38·73	32·63
Fibre	17·50	23·73	24·09
Ash	3·20	6·62	5·20
	100·00	100·00	100·00
Nitrogen	2·93	1·71	2·22

The acrid principle was separated by Thresh (Ph. [3] 309, 941; [3] 315, 21; [3] 326, 259; [3] 7, 473), and named by him *capsaicin* $C_9H_{11}O_5$. It is in the form of minute crystals, melting at 55·5°C., volatilises unchanged at 115°, and at 120° becomes brownish-black. It may be obtained by exhausting cayenne by petroleum, evaporating the petroleum, and treating the extract by dilute solutions of potash. On now saturating the solution with carbonic anhydride, it is precipitated in very small crystals. Its sp.gr. is 1·060. It would appear that capsaicin is not contained in the substance of the seed, for, if the pericarp is carefully separated, the seeds are entirely devoid of acrid taste.

PEPPER OIL *v.* Oils, essential.

PEPPER RESIN *v.* Resin.

PEPPERMINT. The *Mentha piperita* of Europe and America; *M. arvensis* of Japan. Extensively grown for the sake of its volatile oil, which is procured by distilling its leaves. The oil and the preparations made from it are used as aromatics, carminatives, and stimulants, and are useful in medicine for griping pains. It is also employed in the form of mint-camphor, or menthol, for outward application in affections of the nerves.

Oil of peppermint amounts on the average to 0·8 of the total plant used. The crystals of peppermint camphor are obtained from the distillate by cooling; the oil having been drained off, the process is repeated, when a tolerably pure oil is secured. After a third repetition no crystallisation takes place.

Menthol, or peppermint-camphor, in its commercial state is a white crystallised mass, melting at about 35°C. and boiling at 210°C. When purified by distillation the melting-point is raised to 42°C. and the boiling-point to 212°.

Menthone $C_{13}H_{10}O$ is a colourless mobile liquid, neutral to test papers, soluble in almost all proportions in alcohol, chloroform, benzene, and carbon disulphide, but insoluble in water. It stands to menthol in a similar relation to that in which camphor stands to borneol, as is shown by the fact that menthol can be reproduced from its ketone $C_{13}H_{10}O$ by a reaction similar to that by which borneol is produced from camphor.

Menthene $C_{10}H_{10}$ is a colourless liquid of an agreeable odour, moderately soluble in ether or alcohol, more so in benzene, turpentine, and petroleum. It may be prepared by heating menthol with zinc chloride. See J. Moss (Ph. [3] 5, 566); J. Mackay (Ph. [3] 5, 825); Beckett and Wright (C. J. 1, 1, 1876); M. Moriya (C. J. 39, 79, 1881); Atkinson and Yoshida (C. J. 41, 49, 1882) (*v. Peppermint camphor*, art. Camphors).

PEPPERMINT CAMPHOR *v.* Camphors.

PEPPERMINT OIL *v.* Oils, essential.

PEPSIN. *Pepsinum; Pepsine* (Fr.); *Pepsin* (Ger.). Pepsin is a ferment, existing in the acid secretion of the mucous membrane of the stomach or gastric juice. It possesses the property, in presence of dilute acid, and, within certain limits of temperature, of converting albuminous food into soluble assimilable peptone. Schwann (Müller's Arch. 1836) made the first attempt to prepare the ferment in a form available for supplying artificial digestion in cases where the natural function was imperfectly performed. To obtain a good product and to preserve it requires great care and skill. The animals generally selected are the hog, sheep, and calf, and the preparation usually employed is simply the dried mucous membrane of the stomach. Details of preparation are given by Beale (N. 3, 207; Med. T. Gaz. 1872, 1, 152), Wasmann (Lehm. Phys. Chem. 2, 40), Brücke (Sitz. B. 43, 601), Schmidt (A. 61, 22), Liebreich (Practitioner, March 1877), Petit (J. Ph. [5] 2, 85), Chapoteaut (C. R. 95, 140), Maly (J. pr. [2] 11, 104), Wittick (J. 1870, 894), Meissner (Z. Rat. Med. 7, 1; 8, 280; 10, 1; 12, 46; 14, 78 and 303), Sundberg (H. 9, 319); also Foster (N. 3, 168), Scheffer (Am. J. Pharm. 42, 98; 43, 3; Ph. [3] 1, 666; 2, 761 and 783), Selldon (Ph. [3] 4, 89), Long (Med. Press. Cir. 8, 300), Kinkead (Lancet, 1870, 2, 667), Farr (Med. T. Gaz. 1871, 1, 302), Rennard (J. 1874, 944), Zwick (Am. J. Pharm. 43, 261), Audouard (Year-Book Pharm. 1878, 343).

Pepsin of commerce varies much in activity (Tuson, Lancet, 1870, 2, 212; Grierson, Year-Book Pharm. 1887, 263). 2 grains added to an ounce of water acidified with 5 minims of hydrochloric acid (sp.gr. 1·16), should form a mixture in which at least 100 grains of finely-divided hard-boiled white of egg will dissolve on being well mixed and stirred for about 30 minutes at 54°. This method of testing, which is adopted by the Pharmacopœia, is the outcome of numerous investigations as to the effect of different temperatures and different forms of albumen, together with the selection of an acid and determination of its appropriate strength. Compare Petit (J. Ph. [5] 1, 82; 2, 85), Benger (Ph. [3] 12, 270 and 415), Grützner (Fr. 1874, 106), Vigier (J. Ph. [5] 9, 398; 9, 461; 10, 17), Mayer (M. S. [3] 13, 842), Schütz (H. 9, 577), Schlickum (Year-Book Pharm. 1886, 96). A. S.

PEPTONES *v.* Albuminoids.

PERFUMES, as applied to the business of the perfumer, consist in odoriferous bodies or extracts, of animal or vegetable origin, or of chemically-prepared imitations of them. Among animal matters are ambergris and the secretions of the civet cat and musk deer. Vegetable products may be either such resinous gums or balsams as benzoin, camphor, myrrh, and opoponax, or the active odorous principle of barks, leaves, and flowers; the chemical bodies employed being *e.g.* coumarin, or coumaric anhydride, nitro-benzol, or false almond, and methyl-protocatechuic aldehyde, or vanillin. For the most part the essences of plants are obtained by distillation and expression, but these means are inapplicable to certain flowers, on the ground that they either do not yield their perfume to these processes at all or yield them in such small quantity as to be practically useless. In this case either *enfleurage* or maceration is resorted to. Both of these are processes which rely on the peculiar capacity which oily matter exhibits in the extraction and retention of odours. *Enfleurage* is practised by laying on trays of grease the flowers whose perfume is desired, renewing the supply as they are deprived of their essence until the pomade has acquired the necessary degree of fragrance. Maceration is resorted to in the case of some flowers which yield their scent more readily when treated with heated fat. From the pomade made by either of these methods the perfume can be extracted by rectified spirit of wine containing 95 p.c. of alcohol (= 60° over proof). The essences so obtained may then be employed by the perfumer either singly or in such combinations as his experience or inventiveness suggest, of which two examples will suffice:—

Lavender Water:

Oil of English lavender . .	8 oz.
Rose water	1 pint
Rectified spirit, 60° o.p. . .	8 pints

Distil to 8 pints.

Eau de Cologne:

Oil of Neroli orange	7 oz.
Essential oil of rosemary	3 ,,
,, ,, orange zest	16 ,,
,, ,, bergamot	3 ,,
Rectified spirit, 60° o.p.	10 galls.

(See The Art of Perfumery, G. W. S. Piesse, Perfumery, in Ency. Brit. and Ure's Dict.)

PERICLINE *v.* Felspar.

PERISTERITE *v.* Felspar.

PERMANGANATES *v.* Manganese.

PERNAMBUCO WOOD *v.* Brazil Wood.

PEROFKITE *v.* Titanium.

PERSEITE $C_7H_{16}O_7$ (Maquenne), a saccharine substance found in the leaves, fruit, and especially in the seeds of *Laurus Persea.* Discovered by Avequin in 1831 and confounded with mannite, from which it is distinguished by its higher melting-point, its crystalline form, and its lack of rotatory power. It is distinguished from dulcite, which fuses at the same temperature, by the fact that it becomes dextrorotatory on the addition of borax to its aqueous solution. To obtain perseite, the bruised seeds are extracted by water at 60° and the liquid mixed with basic lead acetate, filtered, the solution treated with sulphuretted hydrogen and after filtration evaporated to a syrup. On adding methyl alcohol, perseite crystallises out rapidly and may be obtained pure by recrystallisation from water containing methyl alcohol. Perseite fuses at 188°, is readily soluble in warm water, sparingly soluble in cold water. Insoluble in absolute alcohol. Optically inactive, but in presence of borax its aqueous solution becomes strongly dextrorotatory. It forms a heptacetate

$$C_7H_9(C_2H_3O_2)_7,$$

a heptabutyrate $C_7H_9(C_4H_7O_2)_7$ and a heptanitrate $C_7H_9(NO_3)_7$. Treated with hydriodic acid it yields *heptine* C_7H_{12} identical with that contained in resin-spirit (Morris, C. J. 41, 174).

Perseite appears to be an oxymethyl mannite. It is without action on cupropotassium tartrate or on phenylhydrazine, and is unchanged by boiling with dilute acids. Is a heptavalent alcohol, the first known term of the higher homologues of ordinary mannite (Müntz a. Marcano, A. Ch. [6] 3, 279; Maquenne, A. Ch. [6] 19, 5).

PERSIAN-BERRIES. This dye-stuff is the dried unripe fruit of various species of *Rhamnus*, growing wild, or cultivated in Persia, the Levant, and various countries of Southern Europe.

The Persian-berry proper, obtained from *Rhamnus amygdalinus*, *R. oleoïdes*, and *R. saxatilis*, &c., is imported from Smyrna and Aleppo. Its size is about that of a pea, colour yellowish-green, surface much shrivelled, hard, and divisible along well-marked depressions forming a cross, into four parts, each containing a triangular seed; its taste is intensely bitter.

Avignon or French-berries, the product of *R. infectorius* and *R. alaternus*, &c., are smaller in size than the foregoing, and contain only two seeds.

Spanish, Italian, and Hungarian-berries are respectively the products of *R. saxatilis*, *R. infectorius*, and *R. cathartica*. They are similar in appearance and quality to the Avignon-berries. Other qualities come from the Morea, Wallachia, and Bessarabia.

The true Persian-berries are the most highly esteemed, being richest in colouring matter, which resides chiefly in the outer portion. The best qualities are such as have been gathered in an unripe condition, and have a yellowish-green colour; if too yellow, however, they are inferior, having been gathered in a riper condition; while if brown or black they are poor and worthless, being either over-ripe, or injured by damp during long storage.

The greenish-yellow aqueous decoction of Persian-berries soon becomes mouldy on the surface by standing, fermentation takes place, the liquid becomes ropy, an insoluble yellow precipitate is gradually formed, and the solution contains sugar. A similar change soon occurs if Persian-berries are merely steeped in tepid water, and after some time a bright yellow insoluble powder appears in the liquid.

Much of the earlier chemical history of Persian-berries is unsatisfactory, conflicting statements are made by the different investigators, various names are assigned to colouring principles manifestly identical, and so on. The general result of the researches made up to the present, however, is to establish the fact that Persian-berries contain essentially two colouring principles: one a glucoside, *Xanthorhamnin*, very soluble in water and insoluble in ether, and in itself not a dye-stuff; the other, *Rhamnetin*, representing the true colouring matter, is almost insoluble in water, and is produced along with sugar from the former by the influence of fermentation, or of boiling dilute mineral acids. There seem to be evidences also of a peculiar ferment present in the berries specially adapted for effecting the decomposition alluded to.

Xanthorhamnin is prepared, according to Liebermann and Hörmann, by boiling for 8–10 hours, powdered Persian-berries with three times their weight of 85 p.c. alcohol. On standing twenty-four hours, the dark-brown filtered solution deposits a large quantity of the impure glucoside as a brown resinous mass, together with a little free colouring matter. After pouring off the clear solution, it is allowed to stand several days in a cold place, when purer xanthorhamnin separates in the form of pale-yellow cauliflower-like semicrystalline masses, and in such quantity as to congeal the whole liquid to a stiff paste. The total yield of glucoside is about 12–13 p.c. By repeated crystallising from alcohol, and finally from alcohol containing a little water and ether, it may be obtained in distinct crystalline needles. From an aqueous solution it does not crystallise.

Xanthorhamnin is very soluble in water, also in warm alcohol, but is insoluble in ether, benzene, and chloroform. It should be rapidly dried over sulphuric acid in vacuum, and not by heat, since when moist it melts at a low temperature, and acquires a brown colour; but when once dry it may be heated to 130°C. without injury. Its formula, according to Liebermann and Hörmann, is $C_{48}H_{66}O_{29}$. When dried at the ordinary temperature it contains 2 mols. alcohol of crystallisation, which it only loses by heating for some time to 130°C. It reduces Fehling's liquid, also an ammoniacal silver nitrate solution.

Xanthorhamnin possesses the character of an acid or phenolic body. Its aqueous solution when mixed with lead acetate is not precipitated, but merely acquires an orange colour, but on the addition of ammonia (*i.e.* on production of basic lead acetate) it at once gives an orange-coloured precipitate. In caustic alkalis it readily dissolves, with a yellow colour. On mixing its alcoholic solution with a slight excess of alcoholic potash a thick yellow precipitate of the potassium compound of xanthorhamnin ($C_{48}H_{62}O_{29}K_4$) is thrown down.

Xanthorhamnin, first obtained in a crystalline condition by Gellatly in 1858, is essentially the same as the rhamnegin of Lefort, and of Schützenberger and Bertèche. The latter authors distinguish an α and β compound, differing from each other by their solubility in alcohol, and yielding two differently-soluble rhamnetins (α and β), but their existence is by no means sufficiently established.

According to Schützenberger, twelve acetyl groups may be introduced into xanthorhamnin by heating it with acetic anhydride. By fusing it with caustic potash, also by treatment with sodium amalgam, it yields phloroglucin and protocatechuic acid. In the former case there is also produced an acid body, which gives an intense red colouration with alkalis, and similar therefore to the quercetic acid obtained in like manner from quercetin (Smorawski).

Rhamnetin. Boiling dilute acetic acid does not decompose xanthorhamnin, and it may even be dissolved unchanged in hot glacial acetic acid, but if its aqueous solution is even only gently heated in the water-bath with dilute sulphuric acid it is decomposed, and the solution soon becomes turbid through the separation of the colouring matter, rhamnetin, in the form of bright lemon-yellow microscopic needles. The filtered solution contains the sugar termed isodulcite. The change effected, according to Liebermann and Hörmann, may be represented thus:

$$C_{48}H_{66}O_{29} + 5H_2O = 2C_{12}H_{10}O_5 + 4C_6H_{14}O_6.$$

After filtering off the rhamnetin, it is washed with warm water till free from acid, and dried.

Rhamnetin is little soluble even in boiling alcohol, and, indeed in all the ordinary solvents. From phenol, however, it may be crystallised in the form of pale-yellow needles. In caustic potash and soda it readily dissolves with an orange-yellow colour, in ammonia it is less soluble with a yellow colour. In alkaline carbonates it is little soluble, especially in the cold. Its alcoholic solution gives with tin and alum solutions a yellow precipitate, with copper acetate a reddish-brown precipitate, and with lead acetate an orange precipitate.

Rhamnetin appears to be essentially identical with Fleury and Lefort's rhamnin, and with Kane's chrysorhamnin. Bolley's opinion that rhamnetin is identical with quercetin is undoubtedly erroneous, although there is evidently a close relationship existing between these two colouring matters. According to Herzig, rhamnetin is a dimethyl-quercetin. This view is supported by the facts that the highest methyl derivatives obtainable from rhamnetin and from quercetin are identical with each other, and that rhamnetin when heated with hydriodic acid yields methyl-iodide and quercetin. Herzig considers that Liebermann and Hörmann's formula for rhamnetin should be doubled, because of the amounts of phloroglucin and protocatechuic acid it yields on decomposition.

Diacetyl-rhamnetin $C_{12}H_8O_5(C_2H_3O)_2$ is obtained by heating rhamnetin with dehydrated sodium acetate and acetic anhydride. It crystallises from alcohol containing one-tenth glacial acetic acid, in the form of colourless silky needles, m.p. 183–185°C. Herzig considers this substance to be a hexacetyl derivative of the formula $C_{24}H_{10}O_{10}(C_2H_3O)_6$.

Dipropionyl-rhamnetin $C_{12}H_8O_5(C_3H_5O)_2$ is obtained in a similar manner as very pale-yellow needles, m.p. 158–162°C.

Dibenzoyl-rhamnetin $C_{12}H_8O_5(C_7H_5O)_2$ is obtained by treating rhamnetin (1 part) with benzoïc anhydride (4 parts) in a sealed tube for some time at 150°C. It crystallises from glacial acetic acid in the form of colourless silky needles, m.p. 210–212°C.

Dibrom-rhamnetin $C_{12}H_8Br_2O_5$, crystallising from alcohol in yellow needles, is obtained by the action in the cold, of 2 mols. bromine upon 1 mol. rhamnetin suspended in glacial acetic acid. It dyes alumina- or tin-mordanted cotton yellow colours which are more orange in tint than those yielded by rhamnetin.

Dibrom-diacetyl-rhamnetin

$$C_{12}H_6Br_2O_5(C_2H_3O)_2$$

is obtained by heating pure dibrom-rhamnetin with acetic anhydride and dehydrated sodium acetate. It crystallises from alcohol in colourless lustrous needles.

Dimethyl-rhamnetin $C_{12}H_8O_5(CH_3)_2$ is obtained by heating in sealed tube for 10 hours at 120–130°C. xanthorhamnin-potassium with an excess of dehydrated methyl-potassium-sulphate and a little absolute methyl-alcohol. That portion of the product which is insoluble in water crystallises from alcohol in the form of pale-yellow, almost colourless, needles, m.p. 156–157°C.

Rhamnose (*Isodulcite*) ($C_6H_{12}O_5 + H_2O$), provisionally termed rhamnodulcite by Liebermann and Hörmann, is identical with that obtained from quercitrin. It is prepared by heating xanthorhamnin with dilute sulphuric acid, filtering off the precipitated rhamnetin, neutralising the acid filtrate with pure barium carbonate, and evaporating the filtrate from the barium sulphate produced, to a syrupy consistency. The hot syrup is gradually diluted with absolute alcohol as long as a yellow slimy flocculent precipitate is formed; this is filtered off, and the solution then yields, on standing, hard, colourless, lustrous crystals of isodulcite. It is readily soluble in water, also in absolute alcohol. When pure it crystallises with great facility from water. Heated in a capillary tube it softens at 89°C., and melts at 92°–93°C. When very slowly heated in an air-bath it melts even at 70°C. or lower. At 100°–105°C. it loses 1 mol. H_2O, and yields the anhydride $C_6H_{12}O_5$. It rotates a polarised ray slightly to the right. It reduces Fehling's liquid in the same manner as glucose. Impure isodulcite may be fermented by means of yeast, but not when it is pure. Treated with nitric acid it yields oxalic acid and a crystalline acid $C_6H_{10}O_9$. According to Herzig, isodulcite contains the methyl group, since when oxidised with silver oxide it yields acetic acid or acetic aldehyde, according to the amounts of silver oxide employed.

Application.—Persian-berries are chiefly used by calico-printers for the production of bright steam-yellows and oranges, and also greens. For a steam-yellow, alum is added to a freshly-made decoction of the berries, and the mixture is thickened with starch or gum. A small quantity of precipitated stannous hydrate is then added. For a steam-orange the mordant employed is stannous chloride, with the addition of sodium acetate, in order to form stannous acetate, and thus to enable one to add the requisite amount of mordant without tendering the cotton during steaming. The further addition of a small quantity of stannous hydrate may be made. The ingredients of steam-green are: Persian-berry decoction, stannous chloride, alum, acetic acid, potassium ferrocyanide, and sulphuric or oxalic acid, the whole being thickened with gum. All these colours are developed by steaming the printed fabric and finally washing. The steam-yellow and orange made entirely with tin mordant bear moderate soaping very well.

For wool and silk printing, colours similar to the above are employed.

Persian-berry carmine is a bright orange-yellow tin lake, also used by the calico-printer. It is thickened with albumen, and fixed by steaming.

In dyeing, Persian-berries are seldom employed, chiefly, perhaps, because of their comparatively high cost, but also because of the more fugitive character of the bright orange and yellow which they yield with tin and alum mordants, and for which they are chiefly valuable. The analogous colours from quercitron bark are faster to light. On wool, the olives obtained with Persian-berries, copper and iron mordants, are fast to light. Those obtained with chromium mordant are not quite so fast.

Literature.—Fleury, J. Ph. 26, 226; 27, 666; Kane, P. M. 3, 23, 3; Persoz, Traité de l'impression des tissus, 1, 547; Ortlieb, Bull. Mulh. 30, 16; Gellatly, Edin. New. Phil. Journ. 7, 252; Bolley, A. 115, 55; Schützenberger and Bertèche, Bull. Mulh. 35, 455; A. 15, 118; Stein, J. pr. 85, 351; 106, 5; Lefort, C. R. 63, 840, 1082; Liebermann and Hörmann, A. 196, 299, 307; B. 11, 952, 1618; Smorawsky, B. 12, 1595; Hlasiwetz, A. 112, 107; Herzig, Wiener Monatshefte f. Chem. 6, 889; 8, 227; 9, 548; B. 19, 207, 28c.; Fischer, B. 20, 1091; Berend, B. 11, 1353; Will, B. 20, 1186; Liebermann, B. 18, 3414; Ward & Dunlop, Ann. of Botany, 1889.

J. J. H.

PERSIAN GREEN. *Emerald green v.* PIGMENTS.

PERSIAN RED. *Basic lead chromate v.* CHROMIUM.

PERSHITE *v.* FELSPAR.

PERU BALSAM *v.* BALSAMS.

PERUVIAN BARK *v.* VEGETO-ALKALOIDS.

PETALITE *v.* LITHIUM.

PETROFRACTEUR. An explosive resembling *kinetite* (*v.* EXPLOSIVES) in composition, but differing specially in that it contains no guncotton. Is said to consist of a mixture of 10 p.c. nitrobenzene, 67 p.c. potassium chlorate, 20 p.c. potassium nitrate, and 3 p.c. antimony pentasulphide (*v.* Watson Smith, S. C. I. 1887, 5).

PETROLEUM.

American petroleum.

I. OCCURRENCE.

We find in nature three closely related raw materials—natural gas, liquid petroleum, and ozokerite, or natural paraffin. In America all three occur in this association, and the former two have assumed great commercial and technical importance. In this article we confine our attention to the subject of crude petroleum. The producing fields of America may be grouped under seven heads—(*a*) Pennsylvania and New York, (*b*) West Virginia, (*c*) Ohio, (*d*) Kentucky, Tennessee, &c., (*e*) Colorado, (*f*) California, and (*g*) Canada.

Pennsylvania and New York field. This, the first discovered and worked, is still by far the most productive, and furnishes over 90 per cent. of the total annual yield. It covers about 370 square miles, and stretches south-westerly from Alleghany Co., N.Y., to Beaver Co., Pa., on the Ohio river, the development centring about Bradford, in McKean Co., Pa. Beginning at the north, this belt includes what are known as the Alleghany district, Bradford district, Warren and Forest district, Venango district, Butler district, Beaver district, and the Washington district. It had produced up to the end of 1888 346,797,111 barrels (of 42 gals. American) of crude oil. While the oils found in this field may differ considerably in gravity, colour, and undoubtedly in minor chemical characters, ranging from the black oil of Pleasantville to the amber oil of Washington, the differences are not sufficiently fundamental to require different refining treatment, and the oils are gathered by the pipe-lines into two or three groups, such as Bradford, Middle district, and Washington crudes, which are then refined. None of these Pennsylvania and New York oils contains any appreciable amount of sulphur or other impurity which would require special modification of the refining process.

West Virginia field. The production of this field had been for a number of years limited to a heavy oil, which, however, commanded an excellent price as a natural lubricating oil of value. The production was chiefly along the Little Kanawha and Hughes rivers, and the numerous creeks which, like them, are tributary to the Ohio river, and is included in the four counties of Pleasants, Richie, Wirt, and Wood. Within the last two or three years, however, lighter oils as well as gas have been obtained in the counties bordering on the Pennsylvania State line, and a pipe line from Morgantown in Monongalia Co. to the sea-board at Philadelphia has just been completed, and is now operated by the Standard Oil Trust.

Ohio field. At the present time this field ranks second in importance, coming after the Pa. and N. Y. field. That importance has developed since 1885, prior to which year very little relatively had been contributed to the annual production. Both the eastern and the western halves of the State are at present producing oil, but of very different character, and from different geological formations. The Macksburg district, in the eastern part of the State, is producing a light oil resembling the Pa. crude from the Berea grit, while the Lima district, in the north-western part of the State, is producing a black sulphuretted oil, strongly resembling Canadian oil, from the Trenton limestone. Small quantities of heavy oils (also from the Berea grit) are derived in addition from the Mecca and Grafton districts in the eastern and northern parts of the State.

Kentucky and Tennessee field. These States, which have been only partially examined, are not at present producing any notable quantity of oil. A little is obtained near Glasgow, Ky.

Colorado field. The real development of this field began in 1884–85, when a company was organised to work wells already drilled at Florence, and now some six companies are operating. The production in 1888 amounted to 297,612 barrels. The oil-bearing rock of Colorado is, according to Professor Newberry, the Colorado shales, the middle member of the cretaceous group. The Colorado crude has a gravity of about 31°Beaumé.

California field. The production of this field ranks after that of Ohio, and is in many respects quite different from the others already mentioned. It includes, on the one hand, petroleum of 0·844 gravity (39°B.), which, according to Boverton Redwood (S. C. I. 1887, p. 409), yields 15 p.c. naphtha and 45 p.c. kerosene, and on the other hand tar or asphaltum, of gravity 0·990 to 1·10, which latter is not distilled for kerosene, but is utilised for street paving and roofing purposes. The petroleum adapted for refining comes from Sespe, and Santa Paula in Ventura Co., and from Puente and Pico Cañon in Los Angelos Co., and is sent to San Francisco for refining.

Canadian field. The producing oil belt extends from Petrolia in the province of Ontario, in a north-westerly direction, to the township of Sarnia, and in a south-easterly direction to Oil Springs and Euphemia. While the oil from Petrolia and that from Oil Springs differ slightly in gravity (the former being 0·859 to 0·877, and the latter 0·844 to 0·854) all of the Canadian oil contains sulphur, and in the crude state is very offensive in odour. The annual production is variously given, Boverton Redwood (*l.c.*) stating it to be about 700,000 barrels, and Jos. D. Weeks, in 'Mineral Resources of the U.S. for 1888,' giving it on the authority of persons connected with the trade as 868,345 barrels in 1887 and 772,392 barrels in 1888.

II. PRODUCTION AND TRANSPORTATION OF THE CRUDE PETROLEUM.

The oil comes from depths which vary within very wide limits, from the heavy oil strata of West Va. and Ohio, which are from 50 to 60 feet deep, to the producing strata of the Washington Co., Pa., district, which are from 2,400 to 2,600 feet in depth. Many wells, particularly in newly-opened territory where the original gas-pressure has not been lost, are flowing wells, known among oilmen as 'gushers,' and have poured forth in exceptional cases as high as 8,000 and even 9,000 barrels per day. This yield, however, is never long maintained, and declines rapidly until pumping becomes necessary in order to maintain the production of oil. The American oil wells have never even approximated to the prolific yield of some of the Baku oil fountains. The bulk of the production in the American fields is only obtained as the result of systematic pumping. Thus the production of the Pennsylvania and New York field for 1886 was 25,798,000 barrels, an average daily production of 70,679 barrels, obtained from 24,727 producing wells, making the average of production per well per day in 1886 2·80 barrels.

The oil comes usually from well-defined strata of conglomerate, or 'sand rocks,' which are separated by slate or shale rock. These 'oil sands' occur frequently in groups of three, as the Venango first, second, and third sands; the Warren sands; and the Bradford sands. These sands occur at intervals as we go deeper, beginning with the newest geologically, and going down to the older groups. It may happen, too, that in a particular locality the upper sand of a group yields the oil (in which case it is likely to be of heavier character), and in another locality this sand may be barren, while oil is yielded by a lower one. It is rare, however, to find an abundance of oil in several sand rocks of the same geological group.

This article will not allow of a detailed description of the extremely ingenious apparatus now used in boring the American oil-wells, and in fitting them for the production of oil. The accompanying illustration gives a sectional view of the drilling of such a well, and the several strata penetrated (Crew on Petroleum, p. 192).

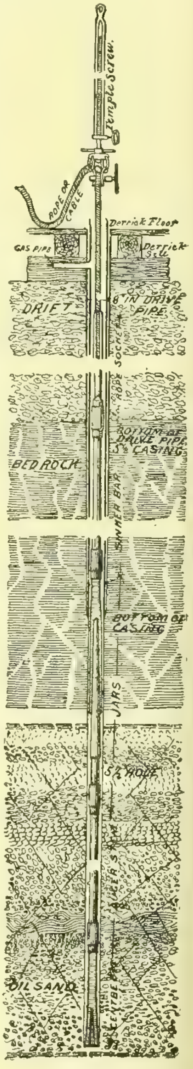

Fig. 1.

'Torpedoes,' or charges of nitro-glycerine, have been largely used in the Pennsylvania and the Canadian fields in order to shatter the oil-sand and open up communication with new portions of the spongy and oil-saturated stratum. The charge in the former locality often rises to 80 or even 100 quarts of nitroglycerine, and in the Canadian field to the tenth part of this amount. The main torpedo is fired by the use of a miniature torpedo or 'squib,' which is run down in contact with the other, and then fired by dropping a weight upon it.

The transportation of crude oil from the wells, which are often in isolated positions, to centrally located storage tanks, and from the points of production to the refineries, is now effected almost exclusively by means of pipe-lines. And as it was found more convenient to locate the great refineries on the Atlantic seaboard, or in large manufacturing centres, the pipe-lines were in time extended so that New York, Philadelphia, Baltimore, Pittsburg, Cleveland, and Buffalo are all connected now with the oil-producing regions of Pennsylvania and New York by long lines of pipe. These great trunk lines, 6 inches in diameter, thus traverse nearly the whole length of the two great States of New York and Pennsylvania, and deliver thousands of barrels of oil daily to refineries on the route and at their different termini on the seaboard. The six great lines referred to as running to the main refining centres are owned by the National Transit Company, an organisation closely connected with the Standard Oil Trust. The New York division consists of two 6-inch pipe-lines, extending from Olean, N.Y., to Bayonne, N.J., and Hunter's Point, N.Y., 312·6 miles in length, with 11 pumping stations for this distance, and has a capacity of 28,000 barrels *per diem.* The pipes are buried at a depth of two or three feet, and follow the general contour of the country through which they pass. The pumps, generally of the Worthington pattern, are powerful machines, and, in order to force the oil such great distances against the friction of the pipes, carry a pressure of from 1,200 to 1,500 lbs. to the square inch. The pipes on the main line are all tested to a pressure of 2,000 lbs. to the square inch. The storage tanks, of which there are two or more at each station, are built of boiler iron, and hold 35,000 barrels each. Obstructions in these lines of pipes are removed by the insertion of a 'scraper' of iron, armed with curved knives, which is driven along by the pressure from the pumps. This is forced from station to station, and is followed by men on foot or horseback, who keep within hearing of the whirring noise of the instrument, and in case of stoppage must locate the spot so as to be able to clear the obstructed section.

The foreign exportation is chiefly of refined oil and other products. A considerable quantity of crude petroleum, however, is exported from the United States to France to be refined there, the French duty on the refined oil encouraging the home refining.

III. Processes of Refining.

As petroleum has been shown to be a mixture of hydrocarbons of different volatility, the first operation would naturally be to effect a partial separation of these hydrocarbons by a process of fractional distillation. But, in fact, simpler lines of treatment were first tried. It was found that crude oils spread out over warm water in tanks and exposed to the sun were much improved in gravity and consistency. This process was chiefly employed for the production of lubricating oils, and the products were called 'sunned oils.' This was followed by the application of methods of partial evaporation or concentration in stills, either by direct application of heat or by the use of steam-coils, carefully avoiding over-heating. The products were called 'reduced oils,' and form the best material for the manufacture of high-grade lubricating oils. They will be referred to again. The process to which the great bulk of crude petroleum is submitted, however, is that of fractional distillation, continued to the eventual coking of the residue. As the most valuable of the several distillates is that which is to be used as illuminating oil, the percentage of that distillate obtainable is an important item in an oil refinery. A normally conducted fractional distillation of Pennsylvania petroleum will give from 35 to 50 p.c. of oil suitable for illuminating purposes, and from 20 to 30 p.c. of lubricating oils. About 1865, however, it was found that if during the distillation the heavy vapours were made to drop back upon the hot oil in the still they became superheated and were decomposed. This process of destructive distillation or 'cracking' allowed of a notable increase of the illuminating oil fraction at the expense of the lubricating oil. So, at present, some 75 to 80 p.c. of burning oil is obtained, while the residuum from which the lubricating oil is obtained is reduced to 6 p.c.

The process of refining crude petroleum is generally divided into two quite distinct parts. The 'benzine' and burning oil distillate are run from the same still, when the fluid residuum is transferred to what are usually called 'tar stills,' in which the rest of the distilling operation is conducted. The crude oil stills are of two forms, the cylindrical still and the 'cheese-box still.' The former, in almost exclusive use at present, consists of a cylinder of boiler-plate, the lower half being generally of steel, 30 feet in length by 12 feet 6 inches in diameter. This still is set horizontally in a furnace of brickwork usually so constructed that the upper half of the still is exposed to the air, which facilitates the cracking in the latter part of the distillation. The 'cheese-box still' has a body and dome-shaped top of boiler-plate and a double curved bottom of steel plate. It is 30 feet in diameter and 9 feet in height and is set on a series of brick arches. The working charge of the cylindrical stills is about 600 barrels, and of the 'cheese-box' stills about double that quantity. Both forms of stills are usually provided with steam pipes both closed and perforated. The steam issuing in jets from the perforated pipe has been found to facilitate distillation by carrying over mechanically the oil vapours.

The condensing apparatus varies somewhat in the details of its construction, but consists essentially of long coils of pipe immersed in tanks through which water is kept flowing. The terminal portions of the condensing pipes all converge and enter the receiving house within a few inches of each other. Near the extremity of each a trap in the pipe is made for the purpose of carrying away the incondensable vapour. This may be allowed to escape or burned underneath the boilers or stills, effecting thereby a large saving in fuel. The condensing pipes generally deliver into box-like receptacles with plate-glass sides, through which the running of the distillate can be observed, and from which test portions can be taken from time to time for the proper control of the process.

The tar-stills are usually of steel, cylindrical in shape, holding about 260 barrels, and are set in groups of two or more, surrounded by brickwork. Vacuum stills have been and are still used to some extent, especially in the preparation of reduced oils, for the manufacture of lubricants and products like vaseline. Of course the evaporation in these stills takes place rapidly, and at the lowest temperature possible, insuring a fractional distillation and not a decomposition. If superheated steam be used, moreover, instead of direct firing, it is possible to reduce oils to 26°B. without any production of pyrogenic products. Continuous distillation has not proved commercially successful in the United States.

To recur now to the products of the first rough distillation of crude oil, the first fraction, known as the 'benzine distillate,' and amounting usually to 12 p.c. of the crude oil, is redistilled by steam heat in cylindrical stills holding 500 barrels, and is sometimes separated into the following products: *cymogene*, 100° to 110°B. gravity; *rhigolene*, 90° to 100°B.; *gasolene*, 80° to 90°B.; *naphtha*, 70° to 76°B.; *benzine*, 62°B. gravity. The time occupied in working the charge is about 48 hours. The percentage of these products varies, but, as a rule, amounts to about 25 p.c. of the first three collectively, rather more than 25 p.c. of the naphtha, and about 40 p.c. of the benzine. The deodorisation of the benzine, which is to be used for solvent purposes in pharmacy or the arts, is effected by the use of sulphuric acid, as in the treatment of the burning oil fraction, only the proportion of acid used is much smaller, and the agitation is effected by revolving paddles instead of by an air-blast. One-half of 1 p.c. is sufficient in this case. Other processes have been proposed for the deodorisation, such as the use of mixtures of sulphuric and nitric acids with alcohol, which produce ethereal products, which are said to neutralise and destroy the benzine odour. The treatment of the illuminating oil fraction is a more important process. It is first subjected to treatment with sulphuric acid, washing with water and a solution of caustic soda. This operation is conducted in tall cylindrical tanks of wrought iron, lined with sheet-lead, which are called 'agitators.' The bottom is funnel-shaped, terminating in a pipe furnished with a stop-cock for drawing off the refuse acid and soda washings. The distillate to be treated must be cooled to at least 60°F., and before the main body of the acid is added for the treatment any water present must be carefully withdrawn. This is done by starting the agitation of the oil by the air-pump and introducing a small quantity of acid. This is allowed to settle and withdrawn. The oil is now agitated and about one-half of the charge of acid is introduced gradually from above. The agitation is now to be continued as long as action is indicated by rise of temperature, when the dark 'sludge acid' is allowed to settle and withdrawn. The remaining portion of the acid is added and a second thorough agitation takes place. The whole charge of acid needed for an average distillate is about 1½ to 2 p.c., or about 6 lbs. of acid to the barrel of oil. The acid as drawn off is dark-blue or reddish-brown in colour and is charged with the sulpho- compounds of the olefines, while the free sulphur dioxide escapes in abundance. The oil after treatment consists of the paraffin hydrocarbons partially freed from admixture with olefines. In colour it has been changed from brownish-yellow to a very light straw shade. The oil is now washed with water introduced through a perforated pipe running round the upper circumference of the tank. This water percolates through the body of the oil, removes the acid, and is allowed to escape in a constant stream from the bottom. When the wash-water shows no appreciable acid taste or reaction the washing is stopped and about 1 p.c. of a caustic soda solution of 12°B. is introduced and the oil is again agitated. When this is drawn off the oil is ready for the settling tanks. A washing with water after the soda treatment sometimes follows, but is not general. A washing with dilute ammonia is also sometimes used to remove the dissolved sulpho- compounds. The settling tanks are shallow tanks, exposed to air and light on the sides, and in these any water contained in the oil settles out and the oil becomes clear and brilliant. The tanks are provided with steam coils for gently warming the oil in cold weather to facilitate this separation. A spraying of the finished oil to raise the fire-test by volatilising a small quantity of the lightest hydrocarbons present is sometimes practised at this stage, but exacter control of the distillation has rendered it no longer necessary.

In the refining of the Canadian oil and the Lima, Ohio, oil, which contains sulphur impurities, after the caustic soda washing, the oil is treated with a solution of litharge in caustic soda, agitation being continued for about 6 hours, or until the oil is deodorised. Sublimed sulphur is then added and the agitation renewed. After the first drawing off of the litharge solution the oil is bleached in sunlight. The oil, however, is not freed from all its sulphur impurity even by this elaborate treatment. More recently it has been found that distillation over finely-divided metallic copper under certain conditions will much more effectually free these oils from the sulphur.

The residuum of the original crude oil distillation is, as was said, distilled from the 'tar-stills.' The first runnings, constituting from 20 to 25 p.c., will have a gravity of 38°B., and are returned to the crude-oil tank for redistillation or are treated and purified as burning oil. The paraffin oil which now runs over may be caught in separate lots, as it deepens in colour and increases in density, or it may be all received together to be treated in the paraffin agitator with acid and purified for the separation of paraffin wax. The agitator in this case must be provided with steam pipes, so that its contents can be kept perfectly liquid, and the charge of acid is larger, amounting to 3, 4, or even 5 p.c. The treatment includes the usual washing with water and soda, all at the proper temperature. The 'sludge' becomes quite solid on standing, and is not worked over. After settling, the paraffin oil goes to the chill rooms, where, by the aid of the ammonia-refrigerating machines and the circulation of cooled brine, the whole mass is brought to a semi-solid condition. This is pressed between bagging by hydraulic pressure, and the refined heavy oil which drains off is collected as lubricating oil. Its gravity should be about 32°B., fire-test 325°F., and cold-test 30°F. The press-cake may be broken up, melted, and recrystallised, and then submitted to still greater pressure at a higher temperature (70°F.) than before, when it is known as 'refined wax.' To convert it into block paraffin it must be washed with benzine, pressed, melted, and filtered through bone-black, when it is obtained perfectly colourless and solidifying to a hard translucent block.

The distillation of residuum is continued until the bottom of the still becomes red-hot, when yellow vapours issue from the tail-pipe and a dense resinous product of a light-yellow colour and nearly solid consistency distils over. This 'yellow wax' contains anthracene and other higher pyrogénic hydrocarbons. Its only use at present is to add it to paraffin oil to increase density and lower cold tests. The coke remaining in the still amounts to about 12 p.c. Reduced oils, obtained by careful driving off of the light fractions of the crude petroleum without cracking, as stated before, are of great value as lubricants. They are generally made by vacuum distillation and the use of superheated steam instead of direct firing. They are either brought into the market at once without further treatment or after a bone-black filtration. This production of filtered oils is usually combined with the manufacture of vaseline or '*petrolatum*,' as it is now known in the U.S. Pharmacopœia. Taking a vacuum residuum as the raw material, this is melted and run on to filters of fine granular well-dried bone-black. The filters are either steam-jacketed or are placed in rooms heated by steam-coils to 120°F. or higher. The first runnings are colourless; and all up to a certain grade of colour go to the manufacture of vaseline. Beyond that the filtrate is known as 'filtered cylinder oil,' and is used as lubricant exclusively.

IV. Character of Products.

The names of commercial products obtained from petroleum have of course been almost infinitely varied, as each manufacturer has his trade names for his special products. We shall only designate the generally accepted classes of products. Beginning with the lightest, we have:—

Cymogene, gaseous at ordinary temperatures, but liquefiable by cold or pressure. Boiling-point 0°C.; sp.gr. 110°Beaumé. Used in the manufacture of ice.

Rhigolene, condensable by the use of ice and salt. Boiling-point 18·3°C., sp.gr. 0·60 or 100°B. Used as an anæsthetic for medical purposes.

Petroleum ether (Sherwood oil), b.p. 70° to 90°C., sp.gr. 0·650 to 0·666 or 85° to 80°B. Used as a solvent for caoutchouc and fatty oils, and for carburetting air in gas machines.

Gasoline (Canadol), b.p. 70° to 90°C., sp.gr. 0·666 to 0·690 or 80° to 73°B. Used in the extraction of oil from oil seeds and in carburetting coal-gas.

Naphtha (Danforth's oil), b.p. 80°–110°C., sp.gr. 0·690 to 0·700 or 73° to 70°B. Used for burning in vapour-stoves and street-lamps, as a solvent for resins in making varnishes, and in the manufacture of oil-cloths.

Ligroïne, b.p. 80° to 120°C., sp.gr. 0·710 to 0·730 or 67° to 62°B. For solvent purposes in pharmacy and for burning in sponge lamps.

Benzine (deodorised), b.p. 120° to 150°C., sp.gr. 0·730 to 0·750 or 62° to 57°B. Used as a substitute for turpentine, for cleansing printer's type, and for dyer's, scourer's, and painter's use.

Burning oil or *Kerosene*. The different burning oils are known often by special names of which the number is legion, but they are graded by the American petroleum exporters chiefly according to the two standards of colour and fire-test, the colours ranging from pale yellow (standard white) to straw (prime white) and colourless (water white). The fire-tests to which the commercial oils are mostly brought are 110°F., 120°F., and 150°F., that of 110° going mainly to the Continent of Europe and to China and Japan, and that of 120° to England. A large proportion of kerosene is now refined on the basis of the Abel test. An oil of 150°F. fire-test and water-white in colour is known in the trade as 'head-light oil.' An oil of 300° fire-test and sp.gr. 0·829 is known as 'mineral-sperm' or 'mineral-colza' oil.

Lubricating oils from petroleum have assumed an importance which is increasing every year. Some crude petroleums like those of Franklin and Smith's Ferry, Pa., Mecca, Ohio, Volcano, W.Va., and other localities, are natural lubricating oils, requiring little or no treatment to fit them for use. The other petroleum lubricating oils are prepared in one of two ways—either by driving off the light hydrocarbons from the crude oil, yielding what is called a 'reduced oil,' or they are the oils obtained by distilling the petroleum residuum in tar stills. The lightest of the lubricating oils, varying in gravity from 32°B. to 38°B., are frequently called 'neutral oils.' They are largely used for the purpose of mixing with animal or vegetable oils, and it is therefore necessary that they should be thoroughly deodorised, decolourised, and deprived of the blue fluorescence or 'bloom.' The first two results are accomplished by bone-black filtration, the last in various ways, such as treatment with nitric acid, addition of small quantities of nitronaphthalenes, &c.

Heavier lubricating oils are called 'spindle' and 'cylinder' oils.

The shipment of refined oils is chiefly in barrels and in cans of tin, two of which latter, holding five gallons American or nearly four imperial gallons each, are packed together in a wooden case. These cases go to China, Japan, and warm climates, as the loss by leakage is less than when the barrel is used. The shipment of oil in bulk for the voyage across the Atlantic presented difficulties so much greater than the shipment in tank steamers on the Caspian that it was not successfully accomplished until within the past few years to London and to Bremen, and now quite a fleet run from Philadelphia and New York to English and German ports. The most important feature of their construction is the provision of auxiliary tanks above the level of the main storage tanks and in communication with them. The storage tanks can thus always be kept full of oil, the auxiliary tanks serving to hold the surplus when the storage tanks become heated and supplying the deficiency when contraction takes place. The 'Crusader' is provided with 40 tanks with an average capacity of 120 barrels each, the 'Andromeda' with 72 tanks, and carried in her first trip to Bremen 684,641 gals. of refined oil.

V. Statistics.

1. *Annual production and value of petroleum in the United States, according to 'Mineral Resources of U.S. Department of Interior'* 1888.

	Production	Value
1882.	30,349,897 barrels	$23,705,698
1883.	23,444,878 "	$25,740,252
1884.	24,214,290 "	$20,476,294
1885.	21,842,041 "	$19,193,694
1886.	28,285,115 barrels	$20,028,457
1887.	28,249,597 "	$18,856,606
1888.	27,615,929 "	$17,950,353

2. *Pipe-line stocks of Penn and New York oil in tanks at close of year (U.S. Mineral Resources* 1888, *and Stowell's Petroleum Reporter).*

	Barrels		Barrels
1882.	34,596,612	1885.	34,428,841
1883.	35,745,632	1886.	34,156,605
1884.	37,366,126	1887.	28,357,112
1888.	18,995,814 + 9,810,714 (Lima oil)		
1889.	11,562,593 + 14,105,149 (Lima oil)		
1890.	10,682,807 + 20,971,395 (Lima oil)		

3. *Exports of Crude and Refined Petroleum from the United States for the years* 1888, 1889, *and* 1890, *according to U.S. Bureau of Statistics.*

—	1888	1889	1890
Crude petroleum exported	77,549,452 gals.*	72,987,383 gals.*	95,350,653 gals.*
Valued at	$5,454,705	$5,083,132	$6,744,235
Naphthas and light distillates	13,481,706 gals.*	14,100,054 gals.*	12,937,433 gals.*
Illuminating oils	455,045,784 "	502,257,455 "	523,295,090 "
Lubricating oils	24,510,437 "	25,166,913 "	30,162,522 "
Residuum and tar	1,870,596 "	1,683,654 "	2,222,472 "
Value of all refined products	$48,105,703	$44,830,545	$44,658,864

* American.

S. P. S.

The Russian Petroleum Industry.

It is difficult to estimate even approximately the number of centuries during which the existence of petroleum in Southern Russia has been known. There can, however, be little doubt that the so-called Eternal Fires at Surakhaneh, on the Apsheron peninsula, have been frequented by fire-worshippers since the commencement of the Zoroastrian period, to which the date of 600 B.C. has usually been assigned, though the temple which now stands in that locality is considered to be of Hindu origin, and is probably not more than two centuries old.[1] The late Mr. Marvin industriously compiled for his interesting work, 'The Region of the Eternal Fire,' an extensive list of references made to the Baku petroleum region by travellers and historians. In Gibbon's Decline and Fall of the Roman Empire it is recorded that Heraclius, having, in A.D. 624, wintered in the Mogan Steppes, at the mouth of the river Kura, 70 miles south of Baku, 'signalised the zeal and revenge of a Christian Emperor. At his command, the soldiers extinguished the fire and destroyed the temples of the Magi.'

Marco Polo, writing in the 13th century, says: 'On the confines towards Georgine, there is a fountain from which oil springs in great abundance, inasmuch as a hundred shiploads might be taken from it at one time. This oil is not good to use with food, but 'tis good to burn, and is also used to anoint camels that have the mange. People come from vast distances to fetch it, for in all the countries round here is no other oil.'[2] With reference to this, Colonel Yule remarks: 'Though Mr. Khanikoff (the celebrated Russian traveller) points out that springs of naphtha are abundant in the vicinity of Tiflis, the mention of *ship-loads* (in Ramusis, indeed, altered—probably by the editor—to *camel-loads*) and the vast quantities spoken of, point to the naphtha wells of the Baku peninsula on the Caspian. Ricold speaks of their supplying the whole country as far as Bagdad, and Barbaro speaks of their practice of anointing camels with oil.' Peter the Great, upon annexing Baku in 1723, made arrangements for the collection of the oil and its transportation up the Volga. A few years later, Baku having meanwhile been restored to Persia, attempts were made by England to establish a trade with India *viâ* the Caspian Sea, and, some complications having arisen, Mr. Jonas Hanway was deputed to proceed to Persia to investigate affairs. Upon his return, Mr. Hanway published, in 1754, An Account of British Trade over the Caspian Sea, wherein the following references to petroleum occur: 'What the Guebers, or Fire-worshippers, call the Everlasting Fire, is a phenomenon of a very extraordinary nature. This object of devotion lies about ten English miles north-east by east from the city of Baku, on a dry rocky land. There are several ancient temples built with stone, supposed to have been all dedicated to fire. Amongst others is a little temple at which the Indians now worship. Here are generally forty or fifty of these poor devotees, who come on a pilgrimage from their own country. A little way from the temple is a low cleft of a rock, in which there is a horizontal gap, two feet from the ground, nearly six long, and about three broad, out of which issues a constant flame, in colour and gentleness not unlike a lamp that burns with spirits, only more pure. When the wind blows, it rises sometimes eight feet high, but much lower in still weather. They do not perceive that the flame makes any impression on the rock. This also the Indians worship, and say it cannot be resisted, but if extinguished will rise in another place. The earth round the place, for above two miles, has this surprising property, that by taking up two or three inches of the surface and applying a live coal, the part which is so uncovered immediately takes fire, almost before the coal touches the earth; the flame makes the soil hot, but does not consume it, nor affect what is near it with any degree of heat. Any quantity of this earth carried to another place does not produce this effect. Not long since, eight horses were consumed by this fire, being under a roof where the surface of the ground was turned up, and by some accident took flame. If a cane or tube even of paper be set about two inches in the ground, confined and closed with earth below, and the top of it touched with a live coal, and blown upon, immediately a flame issues without hurting either the cane or paper, provided the edges be covered with clay; and this method they use for light in their houses, which have only the earth for the floor; three or four of these lighted canes will boil water in a pot, and thus they dress their victuals. The flame may be extinguished in the same manner as that of spirits of wine. The ground is dry and stony, and the more stony any particular part is, the stronger and clearer is the flame; it smells sulphurous, like naphtha, but not very offensive. Lime is burnt to great perfection by means of this phenomenon, the flame communicating itself to any distance where the earth is uncovered to receive it. The stones must be laid on one another, and in three days the lime is completed. Near this place brimstone is dug, and naphtha springs are found. Baku supplies Ghilan and Mazanderan and other countries contiguous with naphtha.' Hanway adds that 'the chief place for the black or dark-grey naphtha' was 'the small island Wetoy, now uninhabited, except at such times as they take naphtha from thence.' The island thus referred to is Sviatoi or Holy Island, which lies at the extremity of the peninsula of Apsheron. Of the Wetoy naphtha, Hanway says: 'The Persians load it in bulk in their wretched vessels, so that sometimes the sea is covered with it for leagues together. When the weather is thick and hazy, the springs boil up the higher, and the naphtha often takes fire on the surface of the earth, and runs in a flame into the sea in great quantities, to a distance almost incredible. In clear weather the springs do not boil up above two or three feet; in boiling over, the oily substance makes so strong a consistency as by degrees to almost close the mouth of the spring; sometimes it is quite closed, and forms hillocks that look as black as pitch, but the spring which is resisted in one place breaks out in another. Some of the springs which have not been long open form a mouth of eight or ten feet diameter. The people carry the naphtha by troughs into pits or reservoirs, drawing it off from one to another, leaving in the first reservoir the water or the heavier part with which it is mixed when it issues from the spring. It is unpleasant to the smell, and used mostly among the poorer sort of the Persians, and other neighbouring people, as we use oil in lamps, or to boil their victuals; but it communicates a disagreeable taste. They find it burns best with a small admixture of ashes. As they obtain it in great abundance, every family is well supplied. They keep it at a small distance from their houses, in earthen vessels underground, to prevent any accident from fire, of which it is extremely susceptible.' Hanway also describes a 'white' variety of naphtha, collected on the peninsula of Apsheron, as 'of a much thinner consistency than black naphtha. The Russians drink it both as a cordial and medicine; but it does not intoxicate. If taken internally it is said to be good for the stone, as also for disorders of the breast, and in venereal cases, and sore heads; to both the last the Persians are very subject. Externally applied, it is of great use in scorbutic pains, gouts, cramps, &c., but it must be put to the part affected only; it penetrates instantaneously into the blood, and is apt, for a short time, to produce great pain. It has also the property of spirits of wine to take out greasy spots in silks or woollens, but the remedy is worse than the disease, for it leaves an abominable odour. They say it is carried into India as a great rarity, and, being prepared as a japan, is the most beautiful and lasting of any that has been yet found.' A third source of petroleum mentioned by Hanway is the island of Tcheleken on the eastern side of the Caspian. Of this island, Captain Woodroffe says: 'We weighed, and came in close under the east side of Naphtonia, as the Russians call it. The Persians call it Cherriken. The coast is difficult of access, being high. It contains about thirty-six families, who have twenty-eight large boats, with several wells of naphtha. The people exist entirely by piracy. To remedy this evil, Nadir Shah, some years ago, offered to forgive all that was past, and to receive them into his favour, if they would come and settle about Astrabad Bay, where they might have lands and sell their naphtha to the inhabitants of that quarter. This they accepted, and carried on a brisk trade for about two years, selling their naphtha to the Persians, Turkomans, &c.; but, getting tired of this way of living, returned to their trade of piracy.'

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[1] When the writer visited Baku in 1884, he found this temple deserted, and the fires extinguished, but he had no difficulty in igniting the gas.

[2] The Book of Ser Marco Polo, the Venetian. Edited by Colonel Henry Yule, C.B., London, 1871.

Russia again annexed Baku in 1801, and the monopoly of producing petroleum was conferred on a trader of the name of Meerzoeff. In 1813 the aggregate yield of the wells was computed to be from 1,000 to 1,500 lbs. per day. From 1821 to 1825 the Government received from Meerzoeff a revenue of 131,000 roubles; and subsequently, up to 1839, from 76,000 to 97,000 roubles per annum, equivalent, at the time, to an average of about 11,000*l.* sterling. During this period the production steadily increased until it amounted to more than a million gallons. From 1832 to 1849 the output from 140 pit wells was as follows:

	Poods. 1 P. = 36·1127 lbs. av.		Poods. 1 P. = 36·1127 lbs. av.
1832 .	. 261,000	1841 .	. 326,695
1833 .	. 300,000	1842 .	. 329,578
1834 .	. 346,109	1843 .	. 327,802
1835 .	. 352,720	1844 .	. 328,280
1836 .	. 352,862	1845 .	. 327,167
1837 .	. 344,147	1846 .	. 332,854
1838 .	. 340,554	1847 .	. 316,850
1839 .	. 358,357	1848 .	. 288,112
1840 .	. 337,010	1849 .	. 255,476

The total revenue from petroleum from 1850 to 1863 amounted to 1,195,000 roubles. From the latter year until 1867 it averaged 162,000 roubles per annum; and thenceforward until 1872, when an excise duty was substituted for the monopoly, 136,000 roubles, the production being as under:

	Poods.		Poods.
1863	340,000	1868	735,764
1864	538,966	1869	1,685,229
1865	554,291	1870	1,704,465
1866	691,820	1871	1,375,523
1867	998,905	1872	1,537,600

In 1872 there were 415 pit wells and two drilled wells.

The abolition of the monopoly had the effect of greatly increasing the production, and Meerzoeff did not long retain a position of supremacy, for in 1873 the Khalify Company struck a flowing well which yielded a large supply; and in the following year the Transcaspian Trading Company, afterwards called the Baku Petroleum Company, took the lead in the business. In 1875 Messrs. Nobel Brothers commenced the systematic production, refining, and transportation of petroleum upon a large scale, and by the introduction of approved appliances for drilling and refining, as well as by the installation of a complete system of pipelines, tank steamers, tank barges, tank railroad waggons, and storage tanks, inaugurated a new era in the Russian petroleum industry.

During the excise duty period the output of crude petroleum was as follows:

	Poods.		Poods.
1873	3,968,000	1876	12,028,000
1874	4,836,000	1877	12,000,000
1875	5,828,000		

At the end of this period there were 130 drilled wells.

The excise duty was removed in 1877, and thereafter, according to the official statistics, the production was as under:

	Poods.		Poods.
1878	15,000,000	1885	116,000,000
1879	21,000,000	1886	150,000,000
1880	25,000,000	1887	165,000,000
1881	40,000,000	1888	192,600,000
1882	50,000,000	1889	205,500,000
1883	60,000,000	1890	239,000,000[1]
1884	90,000,000		

When the writer visited Baku in 1884, the number of drilled wells in the neighbourhood was about 400, but of these only about 100 were producing. At the end of the year 1889 there were 261 producing wells. The average yield per well in the Balakhany-Saboontchi field in 1887 was 762,421 poods, and in 1888 776,794 poods.

Most of the wells are situated in the Balakhany and Saboontchi territories, which are classed as one field. These lands have an area of about four square miles, and occupy a level plateau at an elevation of about 175 feet above the sea. They are distant about eight miles from the town of Baku, which lies on the southern shore of the bay formed by the Apsheron peninsula. About one half of the Balakhany-Saboontchi field has been drilled over, and wells are being sunk in the neighbouring oil territories of Romany and Benegadi, where already successful results have been obtained. It is, however, to the Bibi-Eibat field, which lies two or three miles south of Baku, that attention has lately been largely directed, for the wells which have been drilled here have proved far more productive even than those of the Balakhany-Saboontchi field. At Surakhany, the site of the 'Eternal Fires,' about eleven miles from Baku, petroleum also occurs.

Petroleum is, however, widely distributed throughout Southern Russia, and it will therefore be necessary now to consider the other principal producing localities. From the Crimea eastward through the Taman Peninsula, thence through the Caucasus and into the territory on the farther side of the Caspian Sea, the petroleum deposits are known to extend, and the Apsheron peninsula alone comprises perhaps as much as 12,000 square miles of more or less productive territory.

Colonel Stewart points out that a line of petroleum-bearing strata can be traced in the valleys skirting the northern face of the Caucasus range from the Black Sea coast near Taman to Petrofsk, on the Caspian Sea. Next to the deposits situated in the Kouban district the most important are situated in the valley of the Terek River, near Groznaya. This may be described as the northern zone of petroleum-bearing strata. South of this is what may be called the southern zone, commencing at the seaboard a little north of Batoum, between the second and third stations of the Trans-Caucasian railway.

In the Crimea a considerable number of wells have been drilled, but the yield has been inconsiderable. Mr. Chambers gives the following particulars of the wells in this locality:—

Seven at Chingalek, sixteen miles south of Kertch. Deepest 910 feet. This gave for a short time thirty barrels per day.

Four at Kop-Kootchigan.[1] Deepest 840 feet. Little oil.

One at Temesh, abandoned at a depth of 870 feet.

One at Zamoskaya, twenty-five miles west of Kertch, abandoned at a depth of from 500 to 600 feet.

One at Karamish Kelechi. Depth 690 feet.

Two at Teschevli. Depth 630 and 700 feet.

Colonel Stewart, who visited the Kertch field in 1886, gives the depth of the deepest well at Chingalek as 930 feet, and states that, the lower part being cased with only two-inch pipe, the well choked soon after it began to flow. Two other wells have been drilled at Chingalek to a depth of 604 feet and 844 feet respectively, with a diameter at the bottom of seven inches in each instance. The first of these yielded very little oil and the second none, but it was intended to increase the depth of the latter in the hope of rendering the well productive. At the time of Colonel Stewart's visit a well in course of drilling at Kop Kootchigan had reached a depth of 818 feet. This well had been cased with 8-inch pipe to 328 feet, with 7-inch pipe to 718 feet, and with 6-inch pipe below that. The strata in the Kertch field appear to consist of beds of sand with deposits of clay in which boulders occur, and the drilling is found to present considerable difficulties.

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[1] Of this amount more than 18½ million poods was produced in the Bibi-Eibat field, and more than 1½ million poods in the Romany field, the remainder being the produce of the Balakhany-Saboontchi field.

[1] Colonel Stewart reports that there are in this neighbourhood 112 abandoned wells.

On the Taman peninsula the efforts of the producer have been attended with greater success. The petroleum deposits at Illski, forty-seven miles in a direct line from the port of Novorossisk, on the Black Sea, have long been known to the Cossacks, who collected the material for use as cart grease. In 1864 Colonel Novosiltsoff, who had acquired the monopoly of producing petroleum on the Cossack lands in this locality, commenced drilling for oil on the coast; and subsequently, during the years 1873 to 1875, completed nine wells at Illski.[1] The yield of petroleum was, however, comparatively small, and Colonel Novosiltsoff became involved in financial difficulties. In 1879 a lease of the greater part of the property, which had an area of 1,500,000 acres, was granted for twelve years to Dr. Tweddle, with the exclusive right to drill for petroleum. This right was afterwards transferred by Dr. Tweddle to the Standard Russe Petroleum Company of Marseilles, and the company also acquired a similar right of drilling on an additional 90,000 acres of private lands for periods ranging from twelve to twenty-three years.[2] Of sixty-nine wells drilled at Illski, only one was unproductive, and when Colonel C. E. Stewart visited the district in 1886 fifteen were yielding oil. At Koudako, north of Illski, ten wells have been drilled, and of these four are yielding oil in small quantity. Colonel Novosiltsoff commenced drilling a well in this locality in 1866, and at a depth of only 40 feet obtained from 400 to 500 gallons of oil per day. At a depth of 123 feet the well commenced flowing, and threw up a column of oil 14 feet in height. For a short time the well yielded 5,000 gallons per day, but the bore soon became choked. On the depth then being increased to 182 feet, the well spouted to a height of 40 feet, and discharged 10,000 gallons per day, until it again became choked. The depth was finally increased to 242 feet, when the outflow recommenced with great violence, and enormous quantities of oil are stated to have run to waste. Three other wells were drilled at about the same time, and one of these, with a depth of 343 feet, is said to have yielded by pumping about 60,000 gallons per annum for several years. The Koudako petroleum field is on the estate of General Dourassoff. This estate has an area of about 27,000 acres, of which Colonel Stewart considers at least 5,000 acres to give promise of being rich petroleum territory. The distance from Novorossisk is thirty-five miles by post road, or twenty-two miles in a direct line. Trial borings made on other lands in the vicinity have also been attended in some instances with hopeful results.

Mr. Peacock, in a British consular report, has described in the following terms the petroleum deposits in this neighbourhood: 'Commencing about twenty-two miles north-north-west from the mountain Oshten, and continuing in a north-westerly direction, the first group of the petroleum zone will be the Pshekha-Psish, about twenty miles long. It is the most elevated, and stretches from the valley Pshekha to the left bank of the river Psish. It also comprises the valley of the Tchekokh-Tanko, where is situated the Cossack military station Khodajinskaya, with rich deposits of ozokerit in its close vicinity, and the Cossack station Nephtanaya (meaning in Russian, petroleum village), so called because of numerous natural petroleum pits in the vicinity. About twenty-three miles to the north-west is situated the Pshaf group, nine miles long, and occupying the northern slopes and valleys deviating from an isolated mountain range called Pshaf, and feeding several small streams, of which the Loups, Slitch, and Tchibi are the most remarkable, as rich natural petroleum wells are situated near their courses. In the first of these groups, some trial borings were made several years ago by Colonel Kraftsoff, the deepest of which was bored to 140 feet. A considerable quantity of oil of good quality was obtained from this well, but the work was stopped for want of means. Some of the shallow wells in the Chekokh Valley still yield about 200 gallons a day. In the second group no trial borings have been made. There are only the natural indications.'

In the Tiflis district petroleum occurs near Signakh and at Naftlough. In 1889 the production in the former locality was 55,296 poods (17,000 more than in the previous year). In 1889 the production in the Government of Elisabetpol was 3,000 poods (1,000 more than in the previous year); in Daghestan, 3,955 poods (605 more than in the previous year); and in the province of Terek, 275,721 poods (114,279 more than in the previous year). At Gruzino, near Vladikavkaz, the indications are regarded as particularly promising. The production in the Northern Caucasus for the years 1877 to 1889 is given in an official report as under:—

	Poods		Poods
1877 .	150,000	1884 .	840,000
1878 .	112,000	1885 .	1,140,000
1879 .	200,000	1886 .	1,170,000
1880 .	260,000	1887 .	1,010,000
1881 .	180,000	1888 .	1,412,000
1882 .	470,000	1889 .	1,656,000
1883 .	370,000		

Between the extremity of the Apsheron peninsula and Krasnovodsk on the opposite side of the Caspian Sea extends a submerged mountain ridge, which at one period may have divided the present sea in two. From this ridge at several points petroleum oil and gas rise to the surface of the water and may be ignited. On the Island of Tcheleken, which lies near the Transcaspian coast, there are apparently immense deposits of ozokerit. The soil also appears to be saturated with petroleum, but the trial wells drilled have not been very productive.

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[1] Colonel Stewart states that the deepest of the wells was sunk to 527 feet; at 200 feet it was a flowing well for a short time, and when deepened it yielded by pumping about 2,100 gallons per day. Another well with a depth of 420 feet yielded about 19,000 gallons per day; and a third, which was 460 feet in depth, flowed for a time.

[2] The Standard Russe Company paid rent to the local Cossack Government of [illegible] for the 1,500,000 acres of Cossack lands, and a royalty of two copecks per pood on the crude oil raised.

Of four wells drilled by Messrs. Nobel Brothers one flowed for a short time and afterwards yielded by pumping 500 poods per diem of very heavy oil. The depth of the deepest of these wells was 280 feet. On the mainland beyond the Caspian the existence of petroleum has long been known to the Turkomans, and since 1881 the material has been used as fuel on the railroad. The oil is yielded by three wells of inconsiderable depth which have been drilled at Naphthnia Gora, thirty versts from the Bala Ishen station of the Transcaspian Railway. A narrow-gauge Decauville railway has been laid from the wells to the main line. The quantity of petroleum produced is said not to exceed 600 poods per day. In the same locality there is stated to be a considerable deposit of ozokerit.

The Southern Russian oil deposits extend in a general north-easterly and south-westerly direction, and in the neighbourhood of Baku the dip is said to range from 20° to 40°. According to Vasilieff, practice has justified the recommendation of Professor Romanofsky that wells should not be drilled near the outcrop of the oil-bearing strata, nor at anticlinal bends, but should strike the beds at not less than 400 feet below the outcrop. Vasilieff[1] states that the oil-bearing strata of the Apsheron peninsula belong to the lower Miocene series of the Tertiary epoch. The upper beds, consisting of fossiliferous limestone, have disappeared in the oil-region, the rocks of which are covered by deposits of alluvial origin. The oil-bearing beds are composed of sand, calcareous clays, marls, and in places compact sandstone, often of great thickness, frequently penetrated by beds of pyrites. The calcareous clays are easily bored through. The oil-sands are in a semi-fluid condition when brought to the surface. A characteristic of these oil-bearing rocks is the total absence of organic remains down to the maximum depth yet reached, while the upper beds of the series abound in shells of the Aral-Caspian order. The number of oil-bearing strata is unknown; three have long since been found, but recently a lower oil horizon is stated to have been penetrated at a depth of 1,450 feet. In the Illski district two oil-sands are met with; one at a depth of 200 feet, and the other, which is the more prolific, at from 600 to 1,200 feet below the surface.

In consequence of the strata having been greatly disturbed by volcanic action, drilling in the Apsheron peninsula is difficult and expensive. The progress of the drill is impeded by the occurrence of hard boulders in comparatively soft soil, and 'caving' of the sides of the well is very liable to occur unless the casing closely follows the drill. It is, moreover, impossible to drive the casing of the well to any considerable depth; consequently the size of the hole has as a rule to be several times diminished as the work proceeds, and, unless the well is commenced of large diameter, the size of the bore at the bottom is inadequate. This necessitates the use of very heavy tools and the whole of the drilling appliances need to be of proportionate strength. The derrick employed is a substantial timber structure about seventy feet in height, twenty feet square at the base and about four feet square at the summit. On one side of the derrick stands a massive wooden pillar which carries an oscillating beam. To one end of this beam the drilling tools are suspended, while from the other end a connecting rod passes to a crank actuated by a steam engine through the medium of an endless band. The two principal methods of drilling employed in the Baku fields are known respectively as the rope system and the rod system. In the former the tools are suspended by a cable, while in the latter they are attached to rods of iron or wood. The use of the cable admits of more expeditious drilling, but where the soil is tenacious the employment of rods is held to be preferable if not imperative. The cable system has been gradually growing in favour among drillers in Russia, the increasing depth of the wells accentuating the disadvantage of the rod system. The drilling-tools consist of a chisel-shaped steel-faced bit of the required width, a long stem or rod into which the bit is screwed, a pair of 'jars,' and above the jars another rod. When a cable is used the upper rod is attached to a rope socket holding the end of the drilling cable, and the tools are suspended from the oscillating beam by means of a long screw provided at the lower end with jaws which grasp the cable. Upon the machinery being put in motion the beam to which the tools are suspended commences to oscillate and the drill rising and falling is caused to deliver a succession of blows on the bottom of the well at the rate of forty or fifty a minute. The jars may be likened to two flattened links of a chain, and their function is to deliver an upward stroke to loosen the bit if it should become jammed in the rock. To this end the length of the cable is so adjusted that the jars close a few inches when the bit strikes the bottom of the well. As the drilling proceeds, the screw referred to is rotated and thus the tools are gradually lowered. The driller also at each stroke slightly alters the position of the cutting edge of the bit by twisting the cable. When a depth equivalent to the length of the suspending screw has been drilled or when the bit requires sharpening, the cable, which passes from the jaws of the screw over a pulley at the top of the derrick to a windlass driven by the engine supplying motive power to the beam, is tightened, and, the jaws having been released from the cable, the oscillating beam is disconnected and the tools are drawn from the well. When drilling through dry strata, sufficient water is poured into the well to reduce the detritus to a liquid condition, and upon the withdrawal of the tools the pulverised rock suspended in the water is readily removed by means of the 'sand-pump,' which is a long iron cylinder furnished at the bottom with a valve opening inwards. The bit having meanwhile been dressed, the operation of drilling is recommenced. The weight of the drilling tools commonly exceeds a ton, and the cable is therefore necessarily of great strength, a two-inch plain-laid cable being usually employed. Latterly a wire rope has been successfully substituted for the manilla cable. When rods are employed in lieu of a cable they are generally screwed to the jars without the intervention of the upper iron stem of the cable tools, and are connected to the oscillating beam by means of a chain passing round the barrel of a small winch fixed to the beam, by means of which the tools are gradually lowered as the drilling proceeds. The rods are about 37 feet long, and are made either of ash or of iron. A cable is used to draw the tools from the well (as in the case of cable drilling), and it will readily be understood that as the lengths of rod have to be successively unscrewed and removed during this operation, and reconnected when the tools are again lowered into the well, the operation of drilling occupies more time with pole tools than with cable tools, especially when the well is of considerable depth. The pole system, however, presents the advantage of enabling the driller to rotate the bit in tenacious soil. In what is known as the Fauvelle system, which has been experimentally employed, the rods are hollow, and, a stream of water being forced through them under considerable pressure, the detritus is continuously washed out of the well. In order to prevent caving, the wells are lined with iron casing, which is lowered in successive lengths as the drilling proceeds. The casing is connected by riveting when of considerable diameter, but the lengths of the smaller sizes of casing are screwed together by means of a socket. When the casing with which the well was commenced can no longer be driven any lower, the diameter of the well is decreased by the use of a smaller bit, and a smaller 'string' of casing is inserted, it being frequently found necessary thus to reduce the diameter of the well several times.

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[1] Gorny Jurnal (Russian Mining Journal) 1895. Translated and abstracted by William Anderson, M.I.C.E., and published in the Minutes of Proceedings of the Institution of Civil Engineers, London, 1885.

The diameters of the 261 wells in the Baku district in 1889 were as under:

Inches	Number of wells	Inches	Number of wells
6	13	11	5
6½	1	12	39
7	2	12½	6
7¾	2	14	45
8	31	15	2
8½	2	16	15
9⅛	1	18	13
9½	1	20½	1
9¾	1	21	2
10	61	24	1
10¼	15	?	1
10¾	1		

The time occupied in drilling averages from six to eight months. Occasionally the breakage of the tools in the well or of the cable during the drilling causes great delay, the operation of 'fishing' for the lost tools being frequently one of considerable difficulty.

Mr. Peacock gives the average cost of a well, including labour, derrick, boring tools, pipes for casing, boiler, engine, &c., as 20,000 roubles, or about 2,000*l*. Mr. Chambers states that the cost of a well from 700 to 1,000 feet in depth is not less than 2,000*l*., and that a fair average cost is 2,400*l*. According to Vasilieff the cost of 16 inch, 14 inch, and 12 inch casing pipes for a well in the Baku oil-field, 600 feet deep, amounts to 510*l*., the additional expense for labour being 1,148*l*. 12*s*., or with office charges 1,300*l*. The rates of wages are as follows:—Engine-drivers, with a house, 8*l*. to 10*l*. per month; fitters, 5*s*. per day; turners and smiths, 6*s*. per day; carpenters, 4*s*. per day; labourers, from 1*l*. 16*s*. to 2*l*. per month, except in the case of Persians, who work for 1*l*. to 1*l*. 4*s*. per month. In the Bibi-Eibat field the owner of the land supplies the necessary plant and machinery, the drilling being contracted for at the rate of 10 roubles for the first fathom of seven feet, up to 90 roubles per fathom at the depth of 90 fathoms. The average rate of drilling is asserted by this writer to be 140 feet per month. The various estimates given of the average cost of a well do not include the price of the land. In the Baku district the land generally belongs to the operator, though some leases at a royalty of one third of the production are held. Much of the land originally belonged to the Government, and Mr. Chambers states that leases were granted at merely nominal rental on royalty. Mr. Peacock reports that the following sums were paid for the petroleum lands surrounding Baku:—For 170 desetines of Crown lands, 2,980,000 roubles; for 175 desetines of private lands, 2,028,000 roubles; and for sundry other tracts, about 100 desetines, about 1,000,000 roubles. Tested territory might, however, he adds, be purchased in 1886 at half the price originally paid, and Crown lands on new territories could be leased at the rate of 10 roubles per desetine, or about 2½ acres. Colonel Stewart asserts that plots of the petroleum-bearing lands near Balakhani were granted by the Government without payment to officials and military officers as rewards for services. Some petroleum lands in this district have, however, he adds, a disputed title, being claimed both by the Government and by the peasants. These appear to have been Government lands in Persian times, but, their value not being known, the peasants were allowed to cultivate them and have thus acquired a prescriptive right of ownership.

Tools and machinery were in former years obtained chiefly from foreign countries, but there are now many first-rate workshops in Baku fully capable of supplying the local demand for tools.

The immense pressure which the oil exerts (estimated at as much in some cases as 300 lbs. per square inch) necessitates the provision of special arrangements to prevent the oil from making its way to the surface outside the casing. In some instances an octagonal well about six feet in diameter is sunk about forty feet, or as far as may be necessary to reach solid ground, and the space between the walls of this well and the iron casing is filled in with masonry in cement. In other instances the space is filled with puddled clay after the junction of the casing, and the solid ground at the bottom of the excavated well has been caulked with rope-packing. The average depth of the wells in the Balakhany-Saboontchi field has gradually increased from 420 feet in 1885 to 665 feet in 1889, and Mr. Peacock estimates that the level of the oil in this field is lowered to the extent of 56 feet for every 500 million gallons extracted.

The depths of the 261 wells in the Baku district in 1889 were as follows:

Fathoms of 7 feet	Number of wells
22 to 50	29
50 to 75	54
75 to 100	70
100 to 110	37 (3 fountains)
110 to 120	28 (6 ,,)
120 to 130	23 (6 ,,)
130 to 140	8 (1 ,,)
140 to 150	9 (2 ,,)
150 to 165	2
165 to 168	1

The depth of the wells in the Illski district is, according to Colonel Stewart, from 680 to 1,253 feet, while the diameter ranges from 20 inches at the top to 10 inches at the bottom. In the Kertch field the depth is between 800 and 1,000 feet, and the diameter from 12 inches down to 6 inches, or less.

Upon the oil being 'struck' the well usually commences to spout with great violence, and in order to control the flow an iron cap with gate valve is attached to the casing. Messrs. Nobel Brothers' well No. 32, finished with 8-inch casing in June 1886, required four 8-inch gate valves to stop the flow, and while the well was producing more oil than could be pumped away through three pipes of the respective diameters of 3 inches, 4 inches, and 6 inches, the pressure exerted by the oil was so immense that the valves and strong framework of timbers were blown away, and the well discharged mud, stones, and oil for fifteen days, when the flow ceased. It was estimated that the well ejected during this period about 100,000 barrels of oil, and the cessation of the outflow was believed to be due to the collapse of the casing at the bottom of the well. The celebrated Droojba well spouted with such violence that for four months it was uncontrollable, all attempts to affix a cap being fruitless. The oil column was from 100 to 300 feet in height, and the surrounding country was deluged with the oil. Moreover, the neighbouring engine-houses and workshop were partially buried in the sand ejected with the oil, and many claims were made for the damage thus done. The estimates of the quantity of oil lost ranged from 68,000,000 to 136,000,000 gallons. Mr. Marvin states that the Droojba well spouted for 115 days before it was capped, yielding 3,400 tons a day for 43 days, 1,600 tons a day for 31 days, 900 tons a day for 30 days, and 600 tons a day for 11 days. The Markoff well, not far from the Droojba, spouted in 1887 oil and sand to a height of 400 feet, and on a windy day the oil spray was carried to a distance of eight miles. In the previous year a well drilled by Tagieff ejected for a time 11,000 tons per day.

According to Mr. Chambers, the Mining Company's well, struck in August 1887, at a depth of 790 feet, flowed the full size of the pipe (12 inches) to a height of 200 feet above the derrick for sixty-nine days. The lowest estimate of the production for the sixty-nine days was 3,000,000 barrels, and of this about one-third was lost, the capacity of the available tanks being insufficient. So much sand was thrown up with the oil that some one-story stone buildings, about 15 feet high, within a hundred yards of the well, were buried out of sight, and an area of probably ten acres round the well was covered to a depth of from one to fifteen feet with sand. The production of the well, after sixty-nine days, declined to 200 or 300 barrels per day, and the efforts to resuscitate it were unsuccessful.

When visiting Baku in 1884, the writer saw one of Nobel's capped wells flowing. Upon the opening of the valve the fountain rose to a height of 100 feet with a mighty roar, and continued to play with undiminished violence until the valve was closed, forming a lake of oil to leeward of the derrick.

The following particulars relate to the fountains, or flowing wells, in the Baku district, producing in 1889:

Depth in (7 ft.) fathoms	Diameter in inches	Number of months flowing	Sp.gr. of the petroleum
111[1]	10	4	·878
125	6	5	·884
121[1]	10	2	·887
102	10	3	·865
144[1]	10	4	·878
122[1]	10	4	·865
125[1]	10	4	·865
125	10	3	·868
114	10	3	·870
112	14	4	·872
108	10	2	·863
116	14	2	·873
118[1]	8	6	·886
140	6	9	·854
100	8	4	·899
124[1]	8	5	·876
142	$10\frac{1}{2}$	1	·882
130[1]	6	7	·879

Wells in the Baku field which do not flow cannot be pumped in the ordinary manner in consequence of the large amount of sand present in the oil—sometimes as much as 30 to 40 p.c. The oil is accordingly raised to the surface in cylinders resembling the sand-pump used in drilling. The cylinder commonly holds forty-five gallons, and it is stated that from 18,000 to 20,000 gallons can be thus raised from each well in a working day of 10 hours. At Illski, however, the oil is comparatively free from sand and can be raised with ordinary pumps. In this district a number of wells are pumped by one engine through the medium of rods connected with an oscillating horizontal wheel. According to Vasilieff the average yield of the wells in active work in the Baku district in 1885 was thirty-two tons per well per day. The presence of sand in the oil is attended with considerable practical inconvenience in the case of flowing wells, the iron caps and valves being quickly cut through by the attrition of the sand-laden oil. The ordinary duration of production of the wells may be said to be from two to nine years. The Kormilitza or Wet-Nurse well gave for twelve years 32,000 gallons per day, while Meerzoeff's No. 5 well yielded 40,000 gallons per day for six years.

The crude oil is usually conducted from the wells through wooden troughs into excavated reservoirs where the sand is allowed to deposit.

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[1] Continuous fountains, the others flowing intermittently.

From these reservoirs the oil is piped to the refineries. Up to 1875 the crude oil was transported in barrels by means of Persian carts termed 'arbas.' The arba is a primitive cart with two wheels of great diameter (8½ to 9 feet). The body of the cart held one barrel, and another was slung beneath the axle. Thousands of these carts were in use, and as much as 100,000*l.* per annum was paid for the transport of the oil. The first pipe-line from the wells to the refineries in the Tchorni Gorod or Black Town of Baku, a distance of eight or nine miles, was laid by Messrs. Nobel, and it was found necessary to erect a number of watch-houses in which were stationed armed men to preserve the pipe from destruction by the proprietors of the arbas, who recognised that their industry was threatened with extinction. At the time of the writer's visit to Baku in 1884 there were seven pipe-lines, but the number has been increased to twenty-two. The internal diameter of some of the lines is as much as eight inches.

From the wells at Illski to the refinery at Novorossisk a three-inch pipe-line forty-seven miles in length has been laid. There are five pumping-stations on the line, fitted with Blake pumps, but only three pumps are commonly used, the remaining two being employed only in winter when the oil flows sluggishly.

The specific gravity of Caucasian crude petroleum usually ranges from ·850 to ·875, that of the mixed crude oil from the Balakhany-Saboontchi field being, according to Mr. Chambers, ·865. The colour is commonly dark-brown by transmitted light, while the odour is comparatively slight and not unpleasant. A sample of the remarkable crude petroleum found at Surakhani, submitted to the writer by Colonel Stewart, was of amber colour and of the low sp.gr. of ·780. On the other hand, the writer has received for examination a sample from Tiflis of the density of ·942. This sample was nearly black in colour, almost free from odour, and had a flashing-point of 320°F. (Abel test). Among other samples examined by the writer were the following: A sample marked 'Naphthe léger d'Ilsky,' of sp.gr. ·853, and another of sp.gr. ·942, of brownish black colour, viscid consistency, and having very little odour. One of the Nobel Company's wells, which at first yielded oil of sp.gr. ·860, furnished, on being deepened, oil of sp.gr. ·854, but the specific gravities recorded in the table relating to the fountains in the Baku district in 1889 show that the density of the oil does not in all cases diminish with the increase in depth.

Among the researches which have been instrumental in throwing light upon the chemical composition of Caucasian petroleum may be mentioned those of Beilstein and Kurbatow (Ber. 13, 1813; C. J. 40, 159); Schutzenberger and Jonine (C. R. 91, 823; C. J. 40, 705); Markownikow and Oglobini (C. J. 42, 390; 46, 1276); and Le Bel (C. R. 103, 1017). It has been demonstrated by these chemists that the material consists mainly of hydrocarbons of the C_nH_{2n} series, isomeric both with the olefines, or true homologues of ethylene, and with the hexhydrides of the benzene hydrocarbons, or paraffenes $C_nH_{2n-6}H_6$, obtained synthetically by Wreden. These hydrocarbons, termed naphthenes, closely resemble the paraffins, but are of higher density than their isologues, and boil at slightly lower temperatures than the isomeric olefines and the normal paraffins containing the same number of carbon-atoms, and at approximately the same temperatures as the synthetically prepared paraffenes, as the following examples indicate:—

		Boiling-point
C_8H_{16} (Normal octane)	sp.gr. at 0°C. ·7188	124°C.
C_8H_{16} (Octonaphthene)	sp.gr. at 0°C. ·7714	119°C.
$C_{12}H_{26}$	sp.gr. at 17°C. ·7655	202°C.
$C_{12}H_{24}$	sp.gr. at 0°C. ·8027	196°C.

The naphthenes are attacked by chlorine, forming chlorinated derivatives; but on oxidation are completely destroyed without the formation of characteristic products. The following is a list of the hydrocarbons of this group which have been isolated from Caucasian petroleum:—

	Boiling-point		Boiling-point
C_8H_{16}	119°C.	$C_{12}H_{24}$	196°C.
C_9H_{18}	136°C.	$C_{14}H_{28}$	240°C.
$C_{10}H_{20}$	161°C.	$C_{15}H_{30}$	247°C.
$C_{11}H_{22}$	180°C.		

Caucasian petroleum also contains benzenes (pseudocumene, several isomers of cymene, and of its next homologue) and other benzenoïd hydrocarbons. Neutral and acid oxygenated bodies are also present, Markownikow having found in a fraction boiling between 220° and 230°C. as much as 5·25 p.c. of oxygen.

Solid hydrocarbons only exist as a rule in Caucasian petroleum in very small quantities.

The principal object of the refiner of Russian petroleum has hitherto been to effect the separation and purification of the kerosene or burning oil, this being the most important product. The percentage of kerosene obtainable from the average crude petroleum of the Balakhany-Saboontchi field formerly ranged from 27 to 30 p.c., but improvements in distillation have rendered it possible now to obtain as much as 35 p.c. of a product of satisfactory quality having a sp.gr. of ·825, a flashing-point of 86°F. (Abel test), and a pale-straw colour (nearly equal to the grade of superfine white[1]). The sp.gr. mentioned is much higher than that of United States kerosene, but the Russian oil possesses higher capillary power, and can thus be satisfactorily burned in ordinary lamps when of greater density.

The Caspian Company made, at the time of the writer's visit to Baku in 1884, three grades of kerosene of the following characters:—

	Sp.gr.	Flashing-point	Yield from crude oil
1.	·815	30°C.	20 per cent.
2.	·820	25°C.	33 „ „
3.	·821–·822	22°C.	38 „ „

It is now required that the flashing-point for shipment from Baku shall be not less than 28°C. (Abel test).

The yield of burning oil is therefore comparatively small, and the product is consequently relatively homogeneous. To this fact, the satisfactory burning quality of a product of so high a sp.gr. is no doubt also partly due.

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[1] The colour is described in Baku as not inferior to 2½, superfine white being 2, and prime white 3.

The most volatile products separated at the Nobel refinery at the time of the writer's visit were of the respective sp.grs. of ·754 and ·787. The two products have been termed respectively benzine and gasolene, but the more approximate names of light benzine and heavy benzine are now applied to them. Of these the crude oil yields only a small p.c., but the demand is still smaller. No product of a lower density than ·700 is manufactured in Baku, the crude oil yielding of benzine of sp.gr. ·690, according to Mr. Chambers, less than 1 p.c.

Besides kerosene or ordinary burning oil the crude petroleum yields from 12 to 15 p.c. of a heavy burning oil termed solar oil, or pyronaphtha, having a sp.gr. of about ·865, and a flashing-point of 205°F. (closed test). The yet denser hydrocarbons are to some extent classified by distillation into lubricating oils of various grades, but the residue from the distillation of the kerosene is very largely employed as fuel, the demand for lubricating oils being small in relation to the quantity of material available for their manufacture.

Mr. Chambers has published in a Consular report the following statement of the average results of distillation:—

Illuminating oil .	30	per cent.
Lubricating oil .	20	,, ,,
Solar oil and astatki	35	,, ,,
Waste . . .	15	,, ,,
	100	

The refining of petroleum on the Caspian seaboard is conducted principally in the Black Town of Baku, where in 1889 there were 147 refineries in operation. In 1870 there were only 45 refineries, in 1879 there were 195. In 1885 the number had fallen to 130, the growth of the large refineries in the interval having caused the stoppage of 65 of the smaller ones.

There were also in 1889 the following other refineries in operation:—35 in St. Petersburg and Moscow, eight in the central regions, six in the southern, two in the western, one in the Baltic provinces, one in the northern, one in the south-western, and one in Poland.

The size of the establishments varies greatly. The refineries of the principal firms have a large distilling capacity, but the business of refining is yet to some extent conducted in the huts of the Tartars, where sometimes only a single 10-barrel still may be found. In these primitive Tartar refineries the arrangements for distillation and treatment are imperfect, and the product is consequently of inferior quality, but the establishments of the principal refiners are provided with the most modern appliances. The fuel used is the petroleum residuum, and as this is employed by the smaller refiners by allowing it to burn on the hearth of the furnace, dense volumes of smoke are evolved. To this black cloud, which in certain states of the weather hangs over the neighbourhood of the refineries like a pall, the Black Town (Tchorni Gorod) owes its name. In the larger refineries the liquid fuel is burned by the aid of a steam spray-producer and smokeless combustion is thus obtained.

For the distillation of the kerosene, Nobel Brothers employ a system patented by the late Mr. Ludwig Nobel, whose lamented death was a loss not only to his own Company but to the entire petroleum industry of Russia. The plant adopted in this system consists of a series of connected horizontal cylindrical stills, usually arranged in groups of fourteen, through which the crude petroleum, previously heated, is caused to flow. The stills are heated to carefully-regulated temperatures, corresponding with the volatilising points of the products to be obtained from them. In this manner from the first still of the series, which is the least heated, the most volatile fraction is obtained, the boiling-point and density of the products flowing from the separate condensers connected with the stills increasing with the temperature, until from the last still of the series, which is the most highly heated, the densest fraction which can advantageously be included in the kerosene is collected. From this last still the residuum, which bears the name of astatki, or that of masut, flows into a storage tank. There is a constant flow of heated crude petroleum into the first still, and the process is thus continuous.[1] Mr. Nobel informed the writer that this process is peculiarly suited to the distillation of Caucasian kerosene, for the proportion of this product obtainable is, as already stated, comparatively small, and the material flowing through the stills is therefore not very greatly altered in density by the operation. The stills are usually 22 feet in length by 8 feet in diameter. The kerosene is treated at the Nobel refinery in lead-lined agitators, holding about 57,000 gallons, with about 1½ p.c. of oil of vitriol, the oil being afterwards washed with water, and finally with a solution of caustic soda. The agitation of the oil with the acid, water, and alkali is effected by introducing at the base of the agitator a blast of air. Upon the completion of the treatment the oil is transferred to tanks, in which the complete separation of water is effected, and is then in a fit state for distribution.

The kerosene stills employed by the larger refiners who have not adopted the system of continuous distillation are of the horizontal cylindrical form, and hold over 4,000 imperial gallons. As many as three or four charges are 'run' in 24 hours.

The astatki, or residuum, which commonly has a specific gravity of not less than ·903, is distilled for the production of heavy burning oil and lubricating oils in smaller stills. At one of the largest lubricating oil refineries the distillation is conducted in horizontal cylindrical stills, holding about 8,000 kilos., the charge being worked off in 24 hours, and the distilled products being partially fractionated in air-condensers. The distillation is assisted by the use of superheated steam. The process is usually continued until the distilled product has a sp.gr. of ·915 to ·920, but in some cases the operation is suspended when the distillate has a sp.gr. of ·912, and a further quantity of astatki is added to the residue in the still, it being found that a denser product can thus be obtained. The distillate is fractionated by another distillation, the first and second fractions, which are of the respective sp.grs. of ·865 and ·875, being sold as 'gas oil' and 'cloth oil' respectively, as they are of too little viscosity to admit of their use as lubricants. The next fraction (sp.gr. ·885 to ·895) is sold as 'spindle oil,' the following (sp.gr. ·895 to ·910) as 'machine oil,' and the last (sp.gr. above ·910) as 'cylinder oil.' From the residue in the still a semi-solid product resembling American vaseline is obtained by adding the fraction of ·865 sp.gr. in the proportion of one part to three parts of the residue, and carefully continuing the distillation with the aid of superheated steam. The purification of the lubricating oil distillates is sometimes effected by treating them with from 5 to 10 p.c. of oil of vitriol and afterwards with slaked lime, the process being completed by a final distillation. In other cases, the oil is simply treated with acid and alkali.

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[1] A continuous system of distillation has also been adopted in the Schibaieff refinery.

At the Nobel works the process of continuous distillation is also adopted in the manufacture of lubricating oils, the stills, which are 22 feet in length by 10 feet in diameter, being arranged in groups of nine. The manufacture of paraffin is not carried on in Baku, the crude petroleum containing but a very small percentage (about ¼ p.c.) of solid hydrocarbons, and the lubricating oils requiring no exposure to a low temperature to effect the separation of such hydrocarbons and thus fit them to resist cold without solidification. According to Mr. Nobel, Caucasian crude petroleum is stated to yield about 5 p.c. of cylinder oil, besides upwards of 30 p.c. of other lubricating oils of less density, and 1 p.c. of vaseline, the remaining 14 p.c. consisting of material suitable for use as liquid fuel. These figures, it will be observed, differ somewhat from those already given on the authority of Mr. Chambers.

The Ragosine Company manufacture the following grades of lubricating oils :—

	Sp.gr.
Extra heavy cylinder oil . .	·920
Dark cylinder oil . . .	·918 to ·920
Cylinder and valve oil . .	·912 ,, ·915
Engine machinery oil . .	·905 ,, ·907

The lubricating oils manufactured by S. M. Schibaieff & Co., Limited, are described as follows :—

	Sp.gr.
Cylinder oil	·911 to ·914
Engine oil	·905 ,, ·908
Spindle oil	·896 ,, ·898
Axle oil	·909 ,, ·914
Fine oil	·865 ,, ·866

Russian lubricating oils have at common temperatures much greater viscosity than American lubricating oils of corresponding density, but suffer a greater diminution in viscosity when subjected to equal increments of temperature. Russian lubricating oils also bear exposure to a lower temperature without solidification, in consequence of the comparative absence of solid hydrocarbons.

The following classification of Russian petroleum products was adopted at the Petroleum Conference held at Baku in 1886 :—

1. Benzine : two sorts, viz.—

(*a*) Light benzine : colourless ; used for manufacturing india-rubber goods, and distilled at a temperature not below 130°C. or 266°F.

(*b*) Heavy benzine : of a pale-yellowish colour, yielding 10 p.c. refuse when distilled at a temperature as high as 150°C. or 302°F.

2. Kerosene : sp.gr. 0·830 ; two sorts—

(*a*) Safe ; flashing-point not less than 25°C. or 77°F.

(*b*) Unsafe ; flashing-point below 25°C. or 77°F.

3. Astralin ; sp.gr. 0·850 ; of a pale-yellowish colour ; flashing-point less than 50°C. or 122°F.

4. Solar oil ; sp.gr. above 0·850, but not exceeding 0·880 ; flashing-point not below 80°C. or 176°F. ; may be of very pale yellowish colour.

5. Lubricating oils ; sp.gr. from 0·880 and upwards.

6. Crude oil ; sp.gr. from 0·850 to 0·880 ; flashing-point below 70°C. or 158°F.

7. Mazut, or crude oil deprived of volatile light substances by exposure to air ; sp.gr. above 0·880 ; flashing-point above 70°C. or 158°F. ; and residue, locally called 'astatki,' flashing-point not below 140°C. or 284°F.

8. The different petroleum products in a solid state—asphalte, ozokerit, &c.

9. Cerezine, paraffin, vaseline.

10. The different greases, varnishes, and mastics derived from petroleum.

The following calculation of the cost of producing kerosene from the crude oil was given by Mr. Peacock in 1886 :—

	Copecks
The production of 1 pood of kerosene requires on the average 3¼ poods of crude oil, at 2 copecks per pood, delivered at the refinery . . .	6½
Sulphuric acid	1½
Caustic soda	½
Labour	4
Total . . .	12½

The residue, amounting to 1½ poods, may be sold as liquid fuel at 2 copecks per pood, yielding 3 copecks to be deducted from the above 12½ copecks. The cost of heating the stills is not included, as allowance is made for that in the quantity of crude oil specified. Interest on capital invested in plant, expenses of wear and tear, &c., are not charged in the statement given.

Colonel Stewart takes 3½ poods of crude oil as required for the production of 1 pood of kerosene. He estimates the cost of this at the well at 7 copecks, and adds 3 copecks for the charge for delivery through the pipe-line to the refinery and other expenses ; thus bringing the cost of the raw material to 10 copecks. The expenses of refining he estimates as 5 copecks, and, deducting 3 copecks as the value of the astatki, he gives 12 copecks as the cost of production of a pood of kerosene at Baku.

The writer has recently had occasion to investigate the matter, and he believes that the following is a fair statement of cost :—

	Copecks
Crude oil, 3½ poods at 2 copecks	7
Cost of refining, including fuel, chemicals, establishment expenses, &c.	5½
	12½
Value of astatki, 1½ poods at 4 copecks	6
Net cost of 1 pood of kerosene delivered in tank-waggons at the refinery	6½

or about ½*d.* per gallon.

The value assigned to the crude oil is its approximate present cost to those who have their own wells.

The astatki or residuum is now very largely used as fuel in Russia, both for steam-generating and in metallurgical operations. The steamers on the Caspian Sea and the locomotives on several lines of railway are driven by the employment of astatki, and, wherever the material can be conveyed sufficiently cheaply, it commands a ready sale. It is usually burned by injecting it into the furnace in a condition of spray by means of a jet of steam, a large number of different forms of 'pulverisers' having been devised for the purpose. Its efficiency is about twice that of an equal weight of coal, and its use is obviously accompanied by a very considerable saving in labour. The subject of the employment of astatki as fuel has been treated by the writer in a paper read before the Society of Chemical Industry,[1] and in the Cantor Lectures on Petroleum at the Society of Arts.[2] The successful employment of astatki as fuel for locomotives is largely due to the labours of Mr. Thomas Urquhart, Locomotive Superintendent of the Grazi-Tsaritzin Railway, South-East Russia, whose valuable papers in *Engineering*, vol. xxxv. (1883), and in the Proceedings of the Institute of Mechanical Engineers for 1884 and 1888, may advantageously be consulted by those who are interested in the subject.

The manufacture of benzene, naphthalene, and anthracene by the destructive distillation of astatki in a cupola regenerative furnace has been satisfactorily carried out experimentally on a somewhat large scale by Messrs. Nobel. By the first operation from 30-40 p.c. of tar, containing from 15–17 p.c. of 50 p.c. benzol, is obtained. By a second destructive distillation of the tar, after the benzol has been separated, 70 p.c. of tar is obtained, containing from 7–10 p.c. of 50 p.c. benzol, 16 p.c. of naphthalene, 2–3 p.c. of dry 'green grease' (or 30 p.c. anthracene) and 24 per cent. of pitch. There is also obtained in the process from each cubic foot of astatki 75–100 cubic feet of gas, having an illuminating power about five times greater than that of coal gas.

As Russia furnishes but little timber suitable for the manufacture of barrels in which American petroleum has until within the past few years been so largely transported, it became necessary, at an early period of the development of the Russian petroleum industry, to make arrangements for the carriage of petroleum in bulk. Accordingly, Messrs. Nobel Brothers, undeterred by the want of success which had attended previous efforts to ship petroleum in tanks, had several tank steamers constructed at Motala in Sweden, and in these vessels, which have a capacity of about 225,000 gallons each, the kerosene refined by this firm at Baku has for several years been safely conveyed to the mouth of the Volga, where it is pumped into tank barges for conveyance up the river. At Tsaritzin, 284 miles above Astrakhan, a large storage station has been established, and here the oil is transferred to tank waggons on the railway, for conveyance to other storage stations in the interior of Russia. Messrs. Nobel's principal tank station is situated at Domnino, near Orel, where this firm has 32 tanks, each holding nearly 600,000 gallons. As the late Mr. Marvin has pointed out, an oil train usually consists of 25 tank waggons, each holding about 2,700 gallons of kerosene, or collectively 67,500 gallons. Each storage tank, therefore, holds about nine train-loads of oil, and it thus requires 288 train-loads to fill the Domnino depot. From this centre, distribution of the oil takes place in winter when the Volga navigation is closed. Other firms have followed the example of Messrs. Nobel.

The tank storage capacity in Russia, exclusive of the tanks in Baku, at the end of 1886 was shown by the following list, compiled for the Minister of Finance, to exceed 100,000,000 gallons:—

	Gallons
Astrakhan	1,350,000
Tsaritzin	31,500,000
Saratoff	9,900,000
Batraki	2,475,000
Nijni Novgorod	7,425,000
Perm	1,350,000
Domnino (near Orel)	18,355,500
Grazi	4,500,000
Moscow	4,500,000
St. Petersburg	3,600,000
Warsaw	2,475,000
Libau	1,224,000
Kieff	621,000
Rostoff on the Don	555,750
Kharkoff	527,400
Odessa	2,700,000
Batoum	20,250,000
Total	113,268,650

The principal outlet for kerosene for export is over the Trans-Caucasian railway to Batoum, where the oil is shipped in bulk and in 'cases.' The latter consist of two tin cans, holding four imperial gallons each, in a wooden case, and have long been employed in the shipment of American oil to countries where the barrel would be an unsuitable package. There are in service on the Trans-Caucasian Railway 4,282 tank-waggons, of which 1,400 belong to the railway company and the remainder to the principal refiners. The Trans-Caucasian Railway having been originally carried over the Suram Pass, with a gradient in some places as much as 1 in 22, the transport was both tedious and costly, and in order to increase the carrying capacity of the railway, a pipe-line 38 miles in length has been constructed between Mikhailovo at the eastern end of the Pass, and Kviril at the western end, the oil being discharged from the tank-waggons into tanks at the eastern end, and pumped over the Pass. A railway tunnel under the Pass has also recently been completed, and this has added greatly to the carrying capacity of the line. Another project for the development of the industry which has received considerable attention is the laying of a pipe-line for crude petroleum from Baku to Batoum, a distance of 560 miles, which would, of course, involve the erection of refineries on the Black Sea, and would have the effect of rendering the astatki available for use as fuel on that sea.

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[1] Journal of the Society of Chemical Industry, vol. iv. (1885), p. 70.

[2] Journal of the Society of Arts, vol. xxxiv. (1886).

The exports of crude petroleum and petroleum products from Baku during the years 1889 and 1890 were as under:—

	1889. Poods	1890. Poods
Viâ Caspian Sea:		
Kerosene	23,839,444	23,212,460
Lubricating oil	347,723	558,130
Benzine	233,026	445,085
Astatki	82,237,035	88,893,700
Crude petroleum	3,531,845	5,534,300
	110,189,073	118,643,675
Viâ Trans-Caucasian Railway:		
Kerosene	37,272,238	44,094,040
Lubricating oil	3,018,327	4,042,770
Benzine	89,256	77,115
Astatki	6,433,407	8,228,000
Crude petroleum	559,900	814,400
	47,373,128	57,256,325
TOTAL EXPORTS:		
Kerosene	61,111,682	67,306,500
Lubricating oil	3,366,050	4,600,900
Benzine	322,282	522,200
Astatki	88,670,442	97,121,700
Crude petroleum	4,091,745	6,348,700
	157,562,201	175,900,000

Since January 27, 1888, petroleum products manufactured in Russia have been subject to the following tax:—

1. Illuminating oils of sp.gr. ·730–·830 and flashing-point below 113°F. (Abel-Pensky test)—40 kopecks per pood.

2. Illuminating oils of sp.gr. greater than ·840–·835, and flashing-point not below 113°F.—30 kopecks per pood.

3. Illuminating oils of sp.gr. below ·830, and flashing-point not below 113°F.—30 kopecks per pood.

The tax is collected at the refineries, and is refunded on all oil exported. At the same date the duty on foreign illuminating oils (petroleum) imported into Russia was increased from 60 kopecks to 1 rouble gold per pood.

THE TESTING OF CRUDE PETROLEUM AND OF PETROLEUM PRODUCTS.

1. **Crude petroleum.**—The examination of crude petroleum which the chemist is called upon to conduct in the laboratory for commercial purposes usually includes the estimation of water and sediment, the ascertaining of the specific gravity, flashing-point, setting-point, and viscosity, and the determination of the percentage and character of the products yielded on fractional distillation.

The natural lubricating oils (crude petroleums) of Pennsylvania, Ohio, West Virginia, and Kentucky are classified by the West Virginia Transportation Company according to density, and are subjected to the following test:—

'In receiving and making delivery of oils shipped by the company, the water and sediment contained therein shall be determined by mixing an average sample with an equal quantity of benzine,[1] and subjecting the mixture to 120°F. in a graduated glass vessel for not less than six hours, after which the mixture cools and settles not less than two hours for light grades, three hours for A grade, four hours for B grade, six hours for C grade, eight hours for D grade, and eighteen hours for heavier grades.' The grades are as follows:—

A. 37·1° Baumé (about ·838 sp.gr.) and lighter.

B. 33° to 37°B. (·859 to ·838 sp.gr.).

C. 31·6° to 32·9°B. (·870 to ·859 sp.gr.).

D. 30·6° to 31·5°B. (·873 to ·872 sp.gr.).

E. 29·6° to 30·5°B. (·877 to ·873 sp.gr.).

F. 28·6° to 29·5°B. (·883 to ·877 sp.gr.).

G. 28·5°B. (·883 sp.gr.) and heavier.

Ordinary crude petroleum, from which kerosene and the other usual commercial products, are manufactured, is in the United States required to conform to the following rule of the New York Produce Exchange, except in regard to density, as to which the restriction has been relaxed, in consequence of the fact that much of the crude petroleum now obtained has a density Baumé below 43°:—

'Crude petroleum shall be understood to be *pure natural oil*, neither steamed nor treated, free from water, sediment, or any other adulteration, of the gravity of 43° to 48°B. (·809 to ·786 sp.gr.).'

In order to determine whether the petroleum is a 'pure natural oil,' a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume, and the density of the several distillates is determined. The following results obtained in the examination of two typical samples indicate the form of the certificate handed to the buyer:

Oil from Parker District. Gravity 46° *Baumé.*

1st Product	72°B.	6th Product	46°B.
2nd ,,	62°B.	7th ,,	42°B.
3rd ,,	57 B.	8th ,,	41°B.
4th ,,	53°B.	9th ,,	42°B.
5th ,,	49°B.		

Oil from Bradford District. Gravity 43° *Baumé.*

1st Product	71°B.	6th Product	41°B.
2nd ,,	60°B.	7th ,,	40°B.
3rd ,,	54°B.	8th ,,	41°B.
4th ,,	49°B.	9th ,,	42°B.
5th ,,	45°B.		

The regular gradation in the densities of the fractions exhibited in the foregoing certificates is taken to be a satisfactory indication that the oil is a natural product.

The examination of a sample of crude petroleum with the object of ascertaining the percentage of commercial products obtainable is not always an easy operation, especially when the quantity available is small. The writer is accustomed to conduct the fractional distillation in a glass retort embedded in sand, and to compare the results obtained with those yielded by samples of crude petroleum, the yield of products from which on the commercial scale is known, but even under these circumstances some experience is needed in certain cases. The difficulties encountered arise from the circumstances that in practice in the United States some of the intermediate hydrocarbons are 'cracked,' and thus converted into kerosene to a larger extent than usually occurs when the distillation is conducted in a small retort in the laboratory, and that, on the other hand, the heavy hydrocarbons composing the lubricating oil are less 'cracked' when properly distilled with the aid of steam on the large scale than when distilled on the small scale. The determination of the percentage of solid hydrocarbons is also attended with considerable difficulties when the quantity of material operated upon is small. In every case the aim should be to reproduce as far as possible the conditions of practical working.

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[1] In the case of the more viscous descriptions of petroleum, the writer finds that further dilution is desirable. The benzine used should be fully hydrated.

2. **Petroleum spirit.** In the testing of petroleum spirit, including gasoline, benzine, &c., it is usual to determine the specific gravity and boiling-point, and it is sometimes desirable to make a fractional distillation of the material. Deodorised American petroleum spirit should have no disagreeable odour either in bulk or when evaporated on the hand. A small quantity evaporated in a basin over the water-bath should leave no oily residue. When petroleum spirit is used as a turpentine-substitute in paints it is important that it should contain no sulphur compounds. For the detection of these Allen[1] recommends that the sample be boiled for a few minutes with alcohol and a few drops of ammonia, and that nitrate of silver solution be then added, when there should be no brown colouration.

The presence of sulphuric acid may be detected by agitating the spirit with warm water, separating the water (which should exhibit no acid reaction), and adding to it a few drops of barium chloride solution.

3. **Kerosene.** For ordinary commercial purposes the only characteristics which are noted in the examination of kerosene are the colour, the odour, the specific gravity, and the flashing point or fire-test. In certain cases, however, special tests are applied with the object of ascertaining whether the oil is of satisfactory burning quality, is of natural composition, has been properly treated with acid, has been sufficiently washed, and is free from sulphuric acid, sulphonates, and sulphur in other forms.

(*a*) *Colour.*—Formerly it was the practice to estimate the colour of a sample by comparing it with that of a standard sample, the two oils being placed in bottles of the same size. Such a method did not, however, admit of an accurate comparison being made, and in the year 1870 the writer adopted the plan of placing the samples in long glass cylinders which were held in a frame in such manner that the images of the glass bottoms of the cylinders could be viewed side by side in a mirror. This arrangement was found to present marked advantages in the case of a fluorescent liquid like petroleum, but the system was open to the objection that the standard samples were very liable to become altered in colour, and required to be frequently verified and corrected by experts. Moreover, the adoption by the Petroleum Association of London of precise conditions of contract necessitated the provision of a more accurate and unerring test of colour. Accordingly, the Committee of the Petroleum Association decided, under the advice of the writer, to employ an instrument devised by Mr. R. P. Wilson for use with stained glass standards. This apparatus (fig. 2), which has for the past twenty years admirably fulfilled the object in view, consists of two similar tubes, closed at each end by a screw cap carrying a disc of stout glass. These tubes are placed on a stand at a convenient angle above a small mirror, by means of which light is reflected upwards through them. At the upper ends of the tubes is a box containing two pairs of prisms so arranged that the light passing from the mirror is twice reflected, and is thus brought into an eye-piece surmounting the box. One of the tubes is completely filled with the sample of oil to be tested, the length of the column of liquid being sixteen inches, and beneath the other tube, which remains empty, a disc of stained glass is placed. On applying the eye to the eye-piece the circular field is seen to be divided through the centre by a sharp line formed by the junction of the prisms, the two halves being tinted to an extent corresponding with the colour of the oil and that of the standard glass respectively. The glass standards representing the various grades of colour recognised in the trade are prepared by Mr. Robert Redwood. They are five in number, and are thus designated:

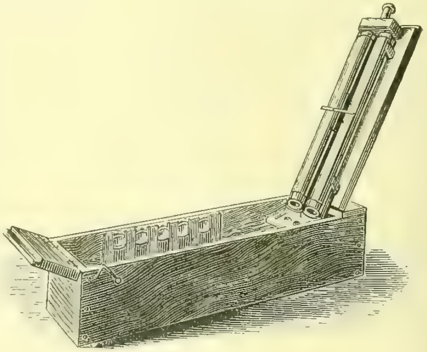

FIG. 2.

1. Water white.
2. Superfine white.
3. Prime white.
4. Standard white.
5. Good merchantable.

The Wilson chromometer admits of an accurate comparison being made, but where the colour of the sample lies between those of two standards, there is an absence of precision in the statement of the result of the test. This has not hitherto been found to be attended with any practical inconvenience where the instrument is simply used for ordinary routine work, but the writer has, during recent years, frequently found it necessary to record the precise colour of a sample, or to state by how much that colour falls short of a stipulated grade. To meet this want a modification of the chromometer already described was designed by Stammer. In this apparatus there is a provision for shortening the length of the column of oil, so that, starting with a standard of somewhat paler tint than the oil, the colour of the oil may be registered in terms of the standard. Messrs. Schmidt and Haensch, the well-known philosophical instrument makers of Berlin, have devoted a good deal of attention to the improvement of Stammer's original instrument, and have devised a colorimeter which the writer has used, and of which he has formed a very favourable opinion. In the construction of this apparatus (fig. 3) Messrs. Schmidt and Haensch have desired to provide for the use of only one glass standard, so that all recorded determinations of colour may be strictly comparable. This would be a distinct advantage, since the relation between the various standards enumerated is a purely arbitrary one; but unfortunately the range of colour is necessarily so wide that if a standard suitable for water-white oil is employed, the column needs to be so much decreased in length for oils of comparatively dark colour that the sensitiveness of the instrument is seriously impaired. To overcome this defect, Mr. Robert Redwood has made several important alterations in the instrument, which, while largely increasing its sensitiveness, admit of the colour of any sample of kerosene being precisely recorded on a scale ranging from water white (1) to good merchantable (5), the space between any two of the colours being divided into ten equal parts, so that the colour of a sample midway between water white and superfine white would be expressed as 1·5. This 'chromograph' has been in use in the writer's laboratory during the past two years, and has given very satisfactory results.

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[1] Commercial Organic Analysis, vol. ii.

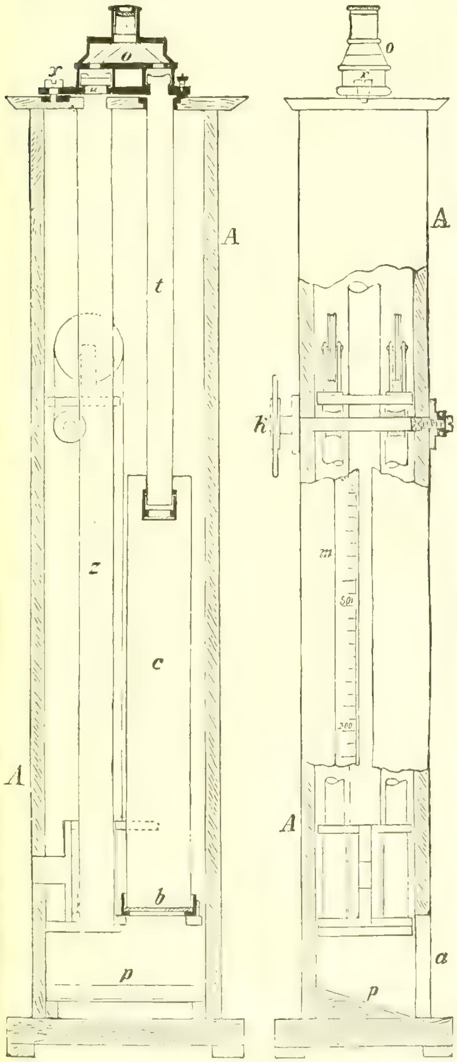

FIG. 3.

A. Case. *a.* Opening for passage of light to reflector. *b, c.* Cylinder, with glass bottom, for oil under examination. *k.* Hand-wheel for raising or lowering cylinder *b, c.* *m.* Graduated scale showing length of column of oil through which light is passing. *o.* Optical arrangement (prisms and eyepiece). *p.* Reflector to project light upwards through the parallel tubes and the prisms into the eyepiece. *t.* Tube closed at the bottom by a glass plate. *u.* Coloured glass disc. *x.* Screw on which the optical arrangement may be turned to insert or remove the disc *u.* *z.* Tube open at both ends.

(*b*) *Odour.*—The determination of odour requires considerable experience, as it is necessarily a matter of judgment, and due consideration has to be given to the origin and grade of the oil. The points to be noticed are whether the odour is indicative of defective refining, and in the case of oil in barrels whether there is evidence in the odour that the glue with which the barrels are coated internally has become decomposed. It is usual to certify that the odour is good merchantable, or not good merchantable, as the case may be.

(*c*) *Specific gravity.*—This is ordinarily determined by the use of a hydrometer, but in the case of oil imported in bulk, where the weight of the oil is calculated from the volume at a given temperature, the writer is accustomed to make use also of the specific gravity bottle.

(*d*) *Flashing-point and fire-test.*—This is, at any rate from one point of view, by far the most important test to which kerosene is subjected, since the petroleum trade is in most parts of the world conducted under legal restrictions in regard to the temperature at which the oil either commences to evolve inflammable vapour or takes fire and continues to burn. The manufacturer of kerosene has on the one hand to avoid introducing into or leaving in the oil such of the more volatile hydrocarbons as would either actually or in the opinion of the Legislature render the fluid unsafe for use in lamps of the ordinary construction, and on the other hand to arrest the collection of the kerosene distillate before the process of distillation has resulted in the addition to the product of the denser hydrocarbons in such quantity as to impair the burning quality. The limitation of the specific gravity was found to be an effectual means of preventing the introduction into the oil of an undue proportion of the denser hydrocarbons, but afforded no check upon the inflammability of the oil; accordingly, in the early days of the petroleum industry, it was customary in the United States to test the oil by pouring it upon warm water and applying a lighted taper to the surface, or by warming the oil in a cup placed in hot water, and applying a flame, the temperature at which the oil gave off ignitable vapour being termed the 'flashing-point,' and that at which it took fire the 'fire-test.' When, however, it became recognised that legal restrictions in regard to the inflammability of kerosene were necessary in the interests of public safety, special forms of apparatus for the testing of flashing-point and igniting-point were devised. The earliest of these testing instruments, known as Tagliabue's open cup-tester (fig. 4), was constructed by an instrument-maker of that name in New York. It consists simply of a glass cup to hold the oil, placed in a small copper water-bath, heated by a spirit lamp. A thermometer is suspended in the oil, and the temperature is noted at which, on passing a lighted splinter of wood across the surface of the oil, there is either a flash of ignited vapour, or on a further increase of temperature the oil ignites and continues to burn. The English Petroleum Act, passed on July 29, 1862, provided that 'Petroleum for the purposes of this Act shall include any product thereof that gives off an inflammable vapour at less than 100° of Fahrenheit's thermometer.' The method of testing was, however, not defined, and the Act was practically inoperative. Accordingly, on July 13, 1868, an amending Act was passed, which prescribed the form of apparatus and method of testing to be adopted, and defined 'petroleum' for the purposes of the two Acts as including 'all such rock oil, Rangoon oil, Burmah oil, any product of them, and any oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any product of them, as gives off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer.' The prescribed apparatus for testing consists of a slightly conical oil cup of thin sheet-iron, provided with a flat rim, and a raised edge ¼ in. high. Across the cup and fixed to or resting on the edge is a wire, which is thus ¼ in. above the flat rim. The oil-cup is supported by the rim in a tin water-bath. The outer vessel having been filled with 'cold or nearly cold water,' as much of the oil to be tested is poured into the cup as will fill it without flowing over the flat rim, and a thermometer with a round bulb, and so graduated that every 10°F. occupies not less than ½ in. on the scale, is then suspended in the oil so that the bulb is immersed about 1½ in. beneath the surface. A screen of pasteboard or wood of specified dimensions having been placed round the apparatus, a 'small' flame is applied to the bottom of the water-bath, and when the temperature of the oil has reached 90°F., a 'very small' flame is passed across the surface of the oil on a level with the wire, this application of the test-flame being repeated for every rise of 'two or three' degrees in temperature, until a 'pale-blue flicker or flash' is produced. The temperature at which this occurs having been noted, the experiment is repeated with a fresh sample of the oil, withdrawing the source of heat when the temperature approaches that noted in the first experiment, and applying the test-flame at every rise of two degrees.[1]

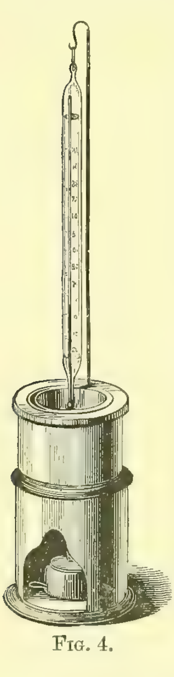

FIG. 4.

The greater part of the earlier petroleum legislation in the United States was based upon fire-test and not upon flashing-point, but in several of the States the petroleum laws now prescribe a test of flashing-point. In 1879 the New York Produce Exchange adopted the Saybolt Electric Tester (fig. 5), which is an open cup instrument wherein the ignition is effected by means of an electric spark from a small induction coil, the spark being caused to pass when required between platinum points at a fixed distance above the surface of the oil. The official directions for the use of the apparatus are as follows :—

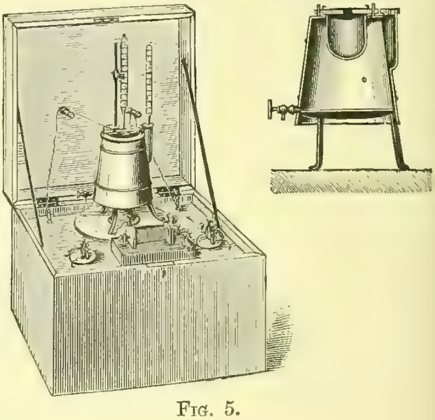

FIG. 5.

'Fill the metal bath with water, leaving room for displacement by the glass cup. Heat the water until the bath thermometer indicates 100°F., at which point remove the lamp. Fill the glass cup with oil to top line, indicated by the rim surrounding cup, which is one-eighth of an inch below top edge of the cup. See that there is no oil on the outside of the cup, nor upon the upper level edge, using paper to clean cup in preference to cotton or woollen material. See that the surface of the oil is free from air bubbles before first flash is produced. Lift the cup steadily with left hand and place in the bath. Suspend the thermometer with the bulb of same immersed just from view under the surface of oil. Adjust the flashing bar and immerse the battery zincs in fluid. Try for first flash every degree until the same is obtained. Attain flash by producing spark with one stroke of the key. The stroke on the key should be such as in telegraphy is used to produce what is called a dot, that is a short quick stroke. The first flash produced from 110° test oil is generally obtained when the temperature of the oil has arrived at 90°. The temperature of the bath at 100° (as per note above) will carry the oil to about 90°, or, in other words, to about the first flashing-point, without the aid of a lamp. When the thermometer in the oil indicates 90°, introduce lamp under the bath, and do not remove until the operation is finished. The temperature of oil when placed in bath should not be lower than 55° nor higher than 70°F. The flashing bar must be free from oil before adjusting for test. Drafts of air must be excluded from the apartment wherein tests are made. Oil of 110° and upwards shall (after first flash) be flashed at 95, 100, 104, 108, 110, 112, 115. Oil of 120° and upwards, after first flash, 100, 105, 110, 115, 118, 120, 122, 125. Oil of 130° and upwards, every five degrees after first flash, until burning-point.'

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[1] The use of the English open-cup instrument, with a test standard of 110°F., was prescribed by law in New South Wales and Queensland, and with a standard of 100°F. in Victoria.

Prior to the introduction of the Saybolt Tester, Arnaboldi constructed an open cup tester similar to Tagliabue's, but of greater capacity, and provided with a mechanical arrangement for passing the test-flame over the oil.

The directions for applying the test given in the English Petroleum Act of 1868 were found to be insufficiently precise, and much difference of opinion existed as to the interpretation of the words 'small flame' and 'very small flame,' with the result that dealers were proceeded against, and in some cases convicted of selling kerosene declared by the local authorities to have a flashing-point below the legal limit of 100°F., but which had been tested by independent experts with satisfactory results. Moreover, the open-cup system of testing was found by experience to be incapable of furnishing trustworthy results in the hands of the comparatively inexperienced and unskilled persons frequently employed by the local authorities.

Accordingly, Mr. Keates, in his capacity of consulting chemist of the Metropolitan Board of Works, suggested the substitution of a closed cup (fig. 6) for the open one, and in 1871 a Bill to legalise this alteration, as well as to amend the law in several other respects, was introduced into Parliament. In consequence, however, of the test standard or limit having been fixed by Mr. Keates at a point (85°) which it was contended was considerably higher than the equivalent of the existing standard, the Bill was opposed by the petroleum trade, and the proposal to change the form of apparatus was withdrawn; the Bill, which passed through the final stage on August 11 in that year, repealing the two previous Acts, but again prescribing the use of the open test specified in the Act of 1868. In the following year the subject of petroleum testing was inquired into by a Select Committee of the House of Lords, and a great deal of conflicting evidence was taken, but no satisfactory conclusion was arrived at. Therefore, in July 1875, with the concurrence and approval of the Metropolitan Board of Works and of the Petroleum Association, Sir Frederick Abel was requested by the Government to undertake an investigation with the object of placing the subject of petroleum testing upon a satisfactory basis. The formulated questions submitted to Sir Frederick Abel were the following:

'1. Whether the method of testing petroleum as prescribed in Schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is such as uniformly to ensure reliable and satisfactory results.

'2. If not, what alterations in the method of testing petroleum should be adopted to secure such results, due regard being had to the fact that the testing must, in many instances, be carried out by persons who have had comparatively little experience in conducting delicate experiments.

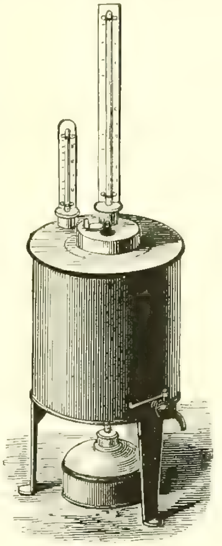
Fig. 6.

'3. Assuming it to be, in your opinion, desirable to obtain a "flashing-test" for petroleum, whether the present "flashing-point" of 100°F. (or its equivalent under any modified method of testing which you may propose) is, in your judgment, calculated to afford adequate protection to the public, without unduly interfering with or restricting the trade; if not, what alteration in this respect should be made.'

After a prolonged and exhaustive experimental inquiry, in which Dr. Kellner rendered valuable assistance, Sir Frederick Abel presented to the Secretary of State an elaborate report, dated August 12, 1876, wherein the questions enumerated were thus answered:

(1.) The method of testing petroleum as prescribed in schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is not 'of a nature uniformly to ensure reliable and satisfactory results.'

(2.) A method of testing petroleum has been elaborated for adoption in place of that prescribed by the Petroleum Act 1871, due regard having been had to the fact 'that the testing must in many instances be carried out by persons who have had comparatively little experience in conducting delicate experiments.' This method, while resembling in its general nature the one hitherto used, is free from the defects inherent in the latter, and is so arranged that it can be carried out, with the certainty of furnishing uniform and precise results, by persons possessing no special knowledge or skill in manipulation. With ordinary attention in the first instance to simple instructions, different operators cannot fail to obtain concordant results with it, and it is so nearly automatic in its nature that it is not, like the present method of testing, susceptible of manipulation so as to furnish different results at the will of the operator.

(3.) There are not, in my judgment, any well-established grounds for considering that the present flashing-point of 100°F. is not 'calculated to afford adequate protection to the public.'

(4.) With the employment of the new test, a minimum flashing-point should therefore be adopted, which is equivalent, or as nearly as possible so, to the flashing-point of 100°F., as furnished by the present test.

It will be obvious that the determination of the equivalent test standard was not an easy part of Sir Frederick Abel's task, since the Abel tester furnishes no exception to the rule that the flashing-point of a given example of petroleum is far lower in a closed than in an open vessel, and it was therefore necessary to deal with the conflicting views already referred to as to the proper mode of conducting the test with the open-cup instrument in order to determine the equivalent standard. The writer was enabled to assist Sir Frederick Abel in the conduct of this portion of the inquiry, but before the test standard was even provisionally fixed, Mr. T. W. Keates, as representing the Metropolitan Board of Works, and Mr. John Calderwood, on behalf of the Scottish Mineral Oil Association, were also consulted. Eventually, as the result of the joint experiments, it was ascertained that the difference between the flashing-points obtained with the open-cup instrument and the Abel tester ranged from 25° to 29°F. Adopting the mean difference of 27°, the new standard was accordingly fixed at 73°F.

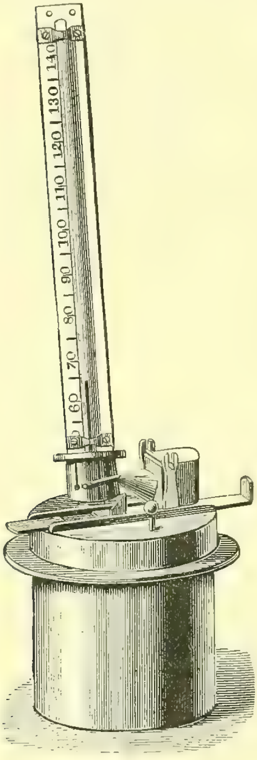

Fig. 7.

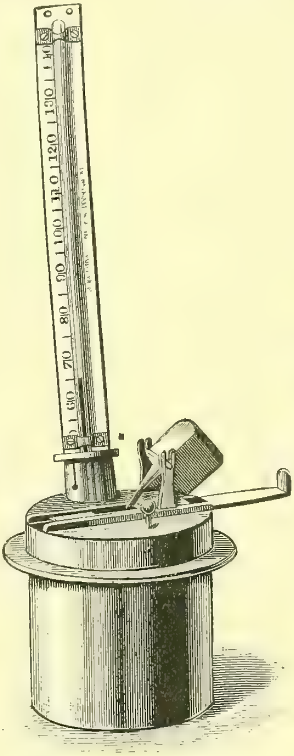

Fig. 8.

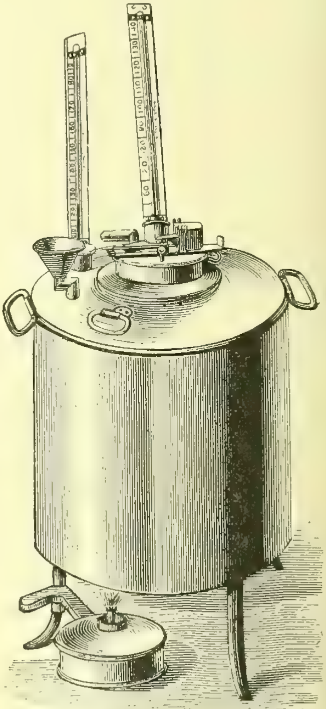

Fig. 9.

After the presentation of the report, the writer proceeded to apply the two tests to 1,000 representative samples of kerosene, with the result that the figures provisionally adopted were confirmed.

The ultimate outcome of Sir Frederick Abel's painstaking investigation was the legalisation by Parliament, on August 11, 1879, of what is now so well known as the Abel Test. The instrument and its use are thus described in the Petroleum Act:—

First Schedule.—Mode of testing petroleum so as to ascertain the temperature at which it will give off inflammable vapour.

Specification of the test apparatus
(figs. 7, 8 and 9).

The following is a description of the details of the apparatus:—

The oil cup (fig. 7) consists of a cylindrical vessel 2″ diameter, $2\frac{2}{10}''$ height (internal), with outward projecting rim $\frac{5}{10}''$ wide, $\frac{3}{8}''$ from the top, and $1\frac{7}{8}''$ from the bottom of the cup. It is made of gun-metal or brass (17 B.W.G.) tinned inside.

A bracket, consisting of a short stout piece of wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is $1\frac{1}{2}''$. The cup is provided with a close-fitting overlapping cover made of brass (22 B.W.G.), which carries the thermometer and test lamp. The latter is suspended from two supports from the side by means of trunnions, upon which it may be made to oscillate; it is provided with a spout, the mouth of which is one-sixteenth of an inch in diameter. The socket which is to hold the thermometer is fixed at such an angle and its length is so adjusted that the bulb of the thermometer, when inserted to its full depth, shall be $1\frac{1}{2}''$ below the centre of the lid.

The cover is provided with three square holes—one in the centre, $\frac{5}{10}''$ by $\frac{4}{10}''$, and two smaller ones, $\frac{3}{10}''$ by $\frac{2}{10}''$, close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves, and having perforations corresponding to those on the lid.

In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the end of the spout just below the surface of the lid (fig. 8). Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position.

Upon the cover, in front of and in line with the mouth of the lamp, is fixed a white bead, the dimensions of which represent the size of the test-flame to be used.

The bath or heating vessel (fig. 9) consists of two flat-bottomed copper cylinders (24 B.W.G.)—an inner one of 3″ diameter and $2\frac{1}{2}''$ height, and an outer one of $5\frac{1}{2}''$ diameter and $5\frac{3}{4}''$ height; they are soldered to a circular copper plate (20 B.W.G.) perforated in the centre, which forms the top of the bath, in such a manner as to inclose the space between the two cylinders, but leaving access to the inner cylinder. The top of the bath projects both outwards and inwards about $\frac{3}{8}''$; that is, its diameter is about $\frac{6}{8}''$ greater than the body of the bath, while the diameter of the circular opening in the centre is about the same amount less than that of the inner copper cylinder. To the inner projection of the top is fastened, by six small screws, a flat ring of ebonite, the screws being sunk below the surface of the ebonite to avoid metallic contact between the bath and the oil cup. The exact distance between the sides and bottom of the bath and of the oil lamp is one-half of an inch. A split socket similar to that on the cover of the oil cup, but set at a right angle, allows a thermometer to be inserted into the space between the two cylinders. The bath is further provided with a funnel, an overflow pipe, and two loop handles.

The bath rests upon a cast-iron tripod stand, to the ring of which is attached a copper cylinder or jacket (24 B.W.G.) flanged at the top, and of such dimensions that the bath, while firmly resting on the iron ring, just touches with its projecting top the inward-turned flange. The diameter of this outer jacket is $6\frac{1}{2}''$. One of the three legs of the stand serves as a support for the spirit lamp attached to it by means of a small swing bracket. The distance of the wick holder from the bottom of the bath is 1″.

Two thermometers are provided with the apparatus—the one for ascertaining the temperature of the bath, the other for determining the flashing-point. The thermometer for ascertaining the temperature of the water has a long bulb and a space at the top. Its range is from about 90° to 190° Fahrenheit. The scale (in degrees of Fahrenheit) is marked on an ivory back fastened to the tube in the usual way. It is fitted with a metal collar, fitting the socket, and the part of the tube below the scale should have a length of about $3\frac{1}{2}''$, measured from the lower end of the scale to the end of the bulb. The thermometer for ascertaining the temperature of the oil is fitted with collar and ivory scale in a similar manner to the one described. It has a round bulb, a space at the top, and ranges from about 55°F. to 150°F.; it measures from end of ivory back to bulb $2\frac{1}{4}''$.

NOTE.—A model apparatus is deposited at the Weights and Measures Department of the Board of Trade.

Directions for applying the flashing-test.

1. The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

2. The heating vessel or water-bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° Fahrenheit, and this is attained in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

If the water has been heated too highly, it is easily reduced to 130° by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

When a test has been completed, this water-bath is again raised to 130° by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

3. The test lamp is prepared for use by fitting it with a piece of flat plaited candle-wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0·15 of an inch diameter, and this size of flame, which is represented by the projecting white bead on the cover of the oil cup, is readily maintained by simple manipulation from time to time with a small wire trimmer.

When gas is available it may be conveniently used in place of the little oil-lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

4. The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65° the samples to be tested should be cooled down (to about 60°) by immersing the bottles containing them in cold water, or by any other convenient method. The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

5. The test-lamp is then placed in position upon the lid of the cup, the lead line or pendulum,[1] which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° the operation of testing is to be commenced, the test flame being applied once for every rise of one degree in the following manner :—

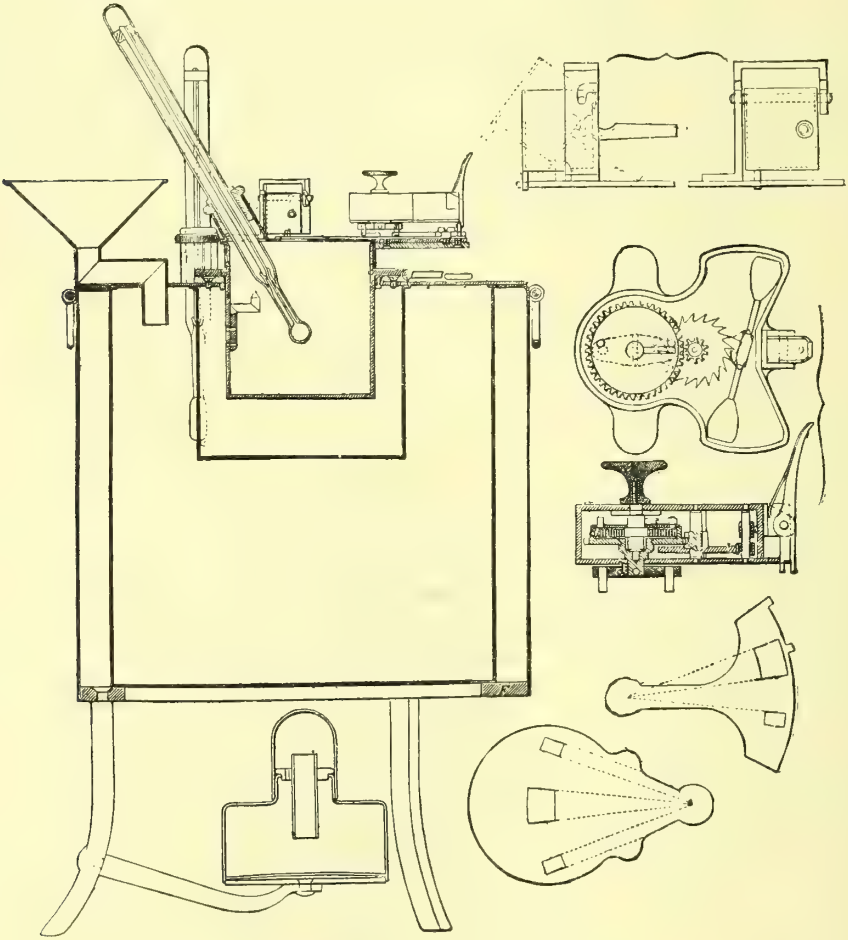

Fig. 10.

The slide is slowly drawn open while the pendulum performs three oscillations and is closed during the fourth oscillation.

Note.—If it is desired to employ the test apparatus to determine the flashing-point of oils of very low volatility, the mode of proceeding is to be modified as follows :—

The air-chamber which surrounds the cup is filled with cold water to a depth of $1\frac{1}{2}$ inches, and the heating-vessel or water-bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus, and kept there during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120° instead of with cold water.

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[1] The pendulum is 24 inches in length from the point of suspension to the centre of gravity of the weight. The writer has found it convenient to employ a synchronised metronome.

In 1880 the subject of petroleum-testing was investigated in Germany by the direction of the Government, and a considerable number of experiments were made with different forms of apparatus. Eventually the Abel instrument was selected as the best, but exception was taken to the personal error liable to be introduced by the method of applying the test-flame, and accordingly a clockwork arrangement for moving the test-slide and bringing the igniting flame to the required position was added (fig. 10). The clockwork movement, which is fixed to the cover of the oil cup, is wound up prior to each application of the test-flame, and is released by pressing a trigger as the mercury in the thermometer reaches each ½°C. The mechanism is so adjusted that the rate of opening and closing the test-orifice is properly timed, and the operator is therefore relieved from the necessity of timing the movement by the aid of a pendulum. The English Abel-apparatus is provided with both oil-lamp and gas arrangement for igniting the vapour, but the German instrument has the oil lamp only, as it was found that the two appliances did not give in all cases concordant results, and petroleum has advantageously been substituted for colza oil for use in the test-lamp.

Before the Abel tester had been very long in use it was found that the results afforded were materially affected by the amount of atmospheric pressure. This source of variation in flashing-point had not previously received attention, and was first accidentally observed in Germany. As the result of a series of experiments conducted in an air-tight chamber in the Jewish Hospital in Berlin at different atmospheric pressures it was found that the difference in flashing-point amounted to about 0·30°C. for 10 mm. in the height of the barometric column, and accordingly a table of corrections was framed on this basis for use with the Abel tester in Germany. With the object of procuring some tangible evidence of the effect of barometric changes upon the flashing-point, the writer conducted, in association with Sir Frederick Abel, a series of tests at different altitudes in Switzerland, and obtained corroborative results, the observed variations in flashing-point being at the rate of 2°F. for 1 inch of barometric pressure. These experiments were, however, not made with a view of determining with precision the extent of variation, the number of tests made in the limited time being too few to justify the basing of a table of corrections on the results.

At a later date an additional source of discrepancies in the results afforded by the Abel instrument was discovered in the effect of a tropical temperature upon the liberation of vapour from the oil. The Indian Government, having adopted the Abel apparatus, had copied verbatim from the English Act the directions for applying the test, and attention was forcibly directed to the source of variations alluded to by the condemnation of several cargoes of kerosene, which had arrived in the port of Calcutta. The writer proceeded to India to investigate the matter, and as the result of experiments made in that country and of a series of tests conducted by Sir Frederick Abel and the writer, with the assistance of Dr. Kellner, in an apartment at Woolwich Arsenal heated to a tropical temperature, it was found that a much lower flashing-point than that furnished in a temperate climate was liable to be obtained when the Abel test was applied in a tropical country in the manner prescribed by the English Act. Further experiments made by Dr. Warden, analyst to the Government of Bengal, Professor Pedler of Calcutta, Dr. Lyon, Sir Frederick Abel, Dr. Kellner, and the writer, showed that the depression of the flashing-point was largely due to the vapour which became disengaged in the act of filling the oil cup. Prolonged cooling of the oil appeared to reduce the liability to this disengagement of vapour, but the only practically available method of eliminating this source of discrepancies was found to be the adoption of some expedient for getting rid of the vapour before commencing the operation of testing or before the flashing-point of the oil was reached. Various methods of effecting this object were tried. The vapour was easily removed by gently blowing over the surface of the oil before placing the cover on the cup, or by the use of an aspirator attached to the cover, or by leaving the test-slide withdrawn for some time; but it was ultimately decided to recommend the commencement of the test many degrees below the flashing-point, so that the disengaged vapour might be removed by the current of air created by the test-flame in successive quantities too small to cause a flash before the volatilisation of the oil began. With this modification in the method of applying the test, the apparatus is caused to give results in a tropical country which agree very closely with those which it furnishes in a temperate climate. Obviously, a portion of the volatile constituents of the oil becomes dissipated in this mode of conducting the test, but, since kerosene cannot be exposed to the air in the tropics without this loss occurring, the defect is not of practical importance. Further details in regard to this question will be found in a joint communication by Sir Frederick Abel and the writer published in the C. N. on May 2, 1884. In October 1887, Sir Frederick Abel drew up the following instructions for the use of the Abel tester in temperate and tropical climates:—

Directions for preparing and using apparatus for testing petroleum oil (these directions apply to the use of the Abel tester in temperate climates):—

1. *Preparing the water-bath.*—The water-bath is filled by pouring water into the funnel until it begins to flow out at the overflow pipe. The temperature of the water at the commencement of each test, as indicated by the long bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in the vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication, or the water is heated by a spirit lamp (which is attached to the stand of the apparatus) until the required temperature is reached.

2. *Preparing the test-lamp.*—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of

adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton-wool moistened with petroleum, any oil not absorbed by the wool being removed. When the lamp has been lighted the flame is adjusted until it is the size of the bead fixed on the cover of the oil-cup.

3. *Filling the oil-cup.*—The oil-cup is placed on a level surface in a good light, and the oil to be tested is poured in without splashing, until its surface is level with the point of the gauge which is fixed in the cup. The oil should be poured from a suitable small vessel, never direct from a large can. The round bulb thermometer is inserted into the lid of the cup, care being taken that the projecting rim of the collar touches the edge of the socket; the test-lamp, prepared as already described, is placed in position, and the cover put on to the cup and pressed down so that its edge rests on the rim of the cup.

4. *The application of the test.*—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the test-flame being compared with that of the bead on the cover. The cup is carefully lifted without being shaken, placed in the bath, and the test-lamp lighted. The thermometer in the oil-cup is now watched, and when the temperature has reached 66°F. (the sample, if necessary, having previously been cooled to below that temperature by immersing the vessel containing it in cold water), the operation of testing is to be commenced, the test-flame being applied once for every rise of one degree.

If the oil-cup is provided with the automatic (Pensky's) arrangement for opening and shutting the slide, the clockwork is wound up by turning the knob from left to right, and set in motion by pressing the trigger.

If the slide is intended to be moved by hand, it should be drawn open slowly and shut quickly. The exact time to be observed in this operation is regulated by the swing of the pendulum supplied with this form of instrument. The opening of the slide should take the time of three oscillations, the shutting of the slide the time of the fourth oscillation of the pendulum. (By one oscillation is meant the passage of the ball of the pendulum from the greatest distance from the vertical on the one side, to the greatest distance on the other.)

If a flash occurs at the first application of the test-flame (at 66°F.), or at any point below 73°F., the operation is to be repeated with a fresh portion of the oil, which is cooled down to 55°F. before being placed in the cup. The first application of the test-flame is made when the temperature of the oil has reached 60°F.

In repeating a test, a fresh sample of oil must always be used, the tested sample being thrown away.

5. *Correction for atmospheric pressure.*—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1·6°F. for every inch of the barometer, a correction of the observed flashing-point may become necessary. The height of the barometer must, therefore, be determined at the time of making the test for the flashing-point. An aneroid barometer is supplied for this purpose. To facilitate the correction of a flashing-point for pressure a table is appended (see table following the directions for applying the test in hot climates), giving the flashing-points of oils ranging from 65–80°F., under pressures ranging from 27–31 inches of mercury.

The table is used in the following manner:—

Example.—An oil has given a flashing-point of 71°, the barometer being 28·6; take the nearest number to 71° in the vertical column headed 28·6. This number is 70·8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of barometer). The substituted number, *i.e.* the true flashing-point of the oil, is 73°.

The following directions apply to the use of the Abel Petroleum Tester in hot climates.

Directions for drawing the sample and preparing it for testing.

1. *Drawing the sample.*—In all cases the testing officer, or some person duly authorised by him, shall personally superintend the drawing of the sample from an original unopened tin or other vessel.

An opening sufficiently large to admit of the oil being rapidly poured or siphoned from the tin or other vessel shall be made.

Two bottles, each of the capacity of about forty fluid ounces, are to be filled with the oil. One of these, the contents of which is intended to be preserved for reference in case of need, is to be carefully corked, the cork being well driven home, cut off level with the neck, and melted sealing-wax worked into it. The other bottle may be either stoppered or corked.

2. *Preparing the sample for testing.*—About ten fluid ounces of the oil, sufficient for three tests, are transferred from the bottle into which the sample has been drawn to a pint flask or bottle, which is to be immersed in water artificially cooled until a thermometer, introduced into the oil, indicates a temperature not exceeding 50°F.

Directions for preparing and using the test apparatus.

3. *Preparing the water-bath.*—The water-bath is filled by pouring water into the funnel until it begins to flow out at the overflow-pipe. The temperature of the water at the commencement of each test, as indicated by the long bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or the water is heated by means of a spirit-lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

4. *Preparing the test-lamp.*—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton wool, moistened with petroleum, any oil not absorbed by the wool

being removed. When the lamp has been lighted, the wick is adjusted by means of a pair of forceps, or a pin, until the flame is the size of the bead fixed on the cover of the oil-cup; should a particular test occupy so long a time that the flame begins to get smaller, through the supply of oil in the lamp becoming exhausted, three or four drops of petroleum are allowed to fall upon the tuft of wool in the lamp from the dropping bottle or pipette provided for the purpose. This can be safely done without interrupting the test.

5. *Filling the oil-cup.*—Before the oil-cup is filled, the lid is to be made ready for being placed upon the cup, *i.e.* the round bulb thermometer is to be inserted into the socket (so that the projecting rim of the collar with which it is fitted touches the edge of the socket), and the test-lamp is to be placed in position. The oil-cup, having been previously cooled by placing it bottom downwards in water at a temperature not exceeding 50°F., is now to be rapidly wiped dry, placed on a level surface in a good light, and the oil to be tested is poured in without splashing until its surface is level with the point of the gauge which is fitted in the cup. The lid is then put on the cup at once, and pressed down so that its edge rests on the rim of the cup.

6. *Application of the test.*—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the entire test-flame being compared with that of the bead on the cover. The cup is carefully lifted, without shaking it, and placed in the bath, the test-lamp is lighted, and the clockwork wound up by turning the key. The thermometer in the oil-cup is now watched, and when the temperature has reached 56° Fahrenheit the clockwork is set in motion by pressing the trigger.

If no flash takes place, the clockwork is at once re-wound, and the trigger pressed at 57° Fahrenheit, and so on, at every degree rise of temperature, until the flash occurs, or until a temperature of 95°Fahrenheit has been reached.

If the flash takes place at any temperature below 77°Fahrenheit the temperature at which it occurs is to be recorded. The fresh portions of the sample are then to be successively tested in a similar manner and the results recorded. If no greater difference than 2°Fahrenheit exists between any two of the three recorded results, each result is to be corrected for atmospheric pressure, as hereafter described, and the average of the three corrected results is the flashing-point of the sample. In the event of there being a greater difference than 2°Fahrenheit between any two of the results, the series of tests is to be rejected, and a fresh series of three similarly obtained, and so on until a sufficiently concordant series is furnished, when the results are to be corrected and the average taken in the manner already described.

No flash which takes place within eight degrees of the temperature at which the testing is commenced shall be accepted as the true flashing-point of the sample tested. In the event of a flash occurring at or below 64° when the test is applied in the manner above described, the next testing shall be commenced ten degrees lower than the temperature at which the flash had been previously obtained—that is to say, at 54° or thereunder, and this procedure shall be continued until the results of three consecutive tests do not show a greater difference than 2°.

If a temperature of 76°Fahrenheit has been reached without a flash occurring, the application of the test-flame is to be continued until a temperature of 95°Fahrenheit has been reached. If no flash has occurred up to this point, and if the petroleum is declared to be imported subject to the provisions of the Act,[1] the tests shall not be continued, and the testing officer shall certify that the petroleum has a flashing-point of over 95° and is not dangerous. But if the petroleum is oil ordinarily used for lubricating purposes, and is declared to have its flashing-point at or above 200°, or is oil to which a notification of the Governor in Executive Council exempting it from the operation of the Act will be applicable in the event of the flashing-point being found to be at or above 120°, the test shall be continued as follows:—The oil-cup is to be removed from the water-bath, and the temperature of the water in the water-bath is to be reduced to 95°Fahrenheit by pouring cold water into the funnel (the hot water escaping by the overflow pipe). The air-chamber is then to be filled to a depth of 1½ inches with water at a temperature of about 95°Fahrenheit, the oil-cup is to be replaced in the water-bath, and the spirit-lamp, attached to the water-bath, is to be lighted and placed underneath. The test-flame is then to be again applied from 96°Fahrenheit, at every degree rise of temperature as indicated by the thermometer in the oil-cup until a flash takes place, or until a temperature of 200°Fahrenheit or 120°Fahrenheit, as the case may be, has been reached. If during this operation the test-flame appears to diminish in size, the lamp is to be replenished in the manner prescribed (at 4) without interrupting the test.

If a flash occurs at any temperature between 76° and 200°Fahrenheit, the temperature at which it occurs, subject to correction for atmospheric pressure, is the flashing-point of the sample.

In repeating a test a fresh sample of oil must always be used, the tested sample being thrown away, and the cup must be wiped dry from any adhering oil, and cooled, as already described, before receiving the fresh sample.

7. *Correction for atmospheric pressure.*—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1·6°Fahrenheit for every inch of the barometer, a correction of the observed flashing-point may become necessary. The height of the barometer must, therefore, be determined at the time of making the test for the flashing-point. An aneroid barometer is supplied for this purpose. To facilitate the correction of a flashing-point for pressure a table is appended, giving flashing-points of oils ranging from 65° to 80°Fahrenheit, under pressures ranging from 27 to 31 inches of mercury.

The table is used in the following manner:—

Example.—An oil has given a flashing-point of 71°, the barometer being at 28·6; take the

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[1] The Indian Petroleum Act is here referred to.

Table for correction of Flashing-points indicated by the Test for Variations in Barometric Pressure on either side of Thirty Inches.

Barometer in inches.																				
27	27·2	27·4	27·6	27·8	28	28·2	28·4	28·6	28·8	29	29·2	29·4	29·6	29·8	30	30·2	30·4	30·6	30·8	31
Flashing Point in Degrees Fahrenheit.																				
60·2	60·5	60·8	61·2	61·5	61·8	62·1	62·4	62·8	63·1	63·4	63·7	64	64·4	64·7	65	65·3	65·6	66	66·3	66·6
61·2	61·5	61·8	62·2	62·5	62·8	63·1	63·4	63·8	64·1	64·4	64·7	65	65·4	65·7	66	66·3	66·6	67	67·3	67·6
62·2	62·5	62·8	63·2	63·5	63·8	64·1	64·4	64·8	65·1	65·4	65·7	66	66·4	66·7	67	67·3	67·6	68	68·3	68·6
63·2	63·5	63·8	64·2	64·5	64·8	65·1	65·4	65·8	66·1	66·4	66·7	67	67·4	67·7	68	68·3	68·6	69	69·3	69·6
64·2	64·5	64·8	65·2	65·5	65·8	66·1	66·4	66·8	67·1	67·4	67·7	68	68·4	68·7	69	69·3	69·6	70	70·3	70·6
65·2	65·5	65·8	66·2	66·5	66·8	67·1	67·4	67·8	68·1	68·4	68·7	69	69·4	69·7	70	70·3	70·6	71	71·3	71·6
66·2	66·5	66·8	67·2	67·5	67·8	68·1	68·4	68·8	69·1	69·4	69·7	70	70·4	70·7	71	71·3	71·6	72	72·3	72·6
67·2	67·5	67·8	68·2	68·5	68·8	69·1	69·4	69·8	70·1	70·4	70·7	71	71·4	71·7	72	72·3	72·6	73	73·3	73·6
68·2	68·5	68·8	69·2	69·5	69·8	70·1	70·4	70·8	71·1	71·4	71·7	72	72·4	72·7	73	73·3	73·6	74	74·3	74·6
69·2	69·5	69·8	70·2	70·5	70·3	71·1	71·4	71·8	72·1	72·4	72·7	73	73·4	73·7	74	74·3	74·6	75	75·3	75·6
70·2	70·5	70·8	71·2	71·5	71·8	72·1	72·4	72·8	73·1	73·4	73·7	74	74·4	74·7	75	75·3	75·6	76	76·3	76·6
71·2	71·5	71·8	72·2	72·5	72·8	73·1	73·4	73·8	74·1	74·4	74·7	75	75·4	75·7	76	76·3	76·6	77	77·3	77·6
72·2	72·5	72·8	73·2	73·5	73·8	74·1	74·4	74·8	75·1	75·4	75·7	76	76·4	76·7	77	77·3	77·6	78	78·3	78·6
73·2	73·5	73·8	74·2	74·5	74·8	75·1	75·4	75·8	76·1	76·4	76·7	77	77·4	77·7	78	78·3	78·6	79	79·3	79·6
74·2	74·5	74·8	75·2	75·5	75·8	76·1	76·4	76·8	77·1	77·4	77·7	78	78·4	78·7	79	79·3	79·6	80	80·3	80·6
75·2	75·5	75·8	76·2	76·5	76·8	77·1	77·4	77·8	78·1	78·4	78·7	79	79·4	79·7	80	80·3	80·6	81	81·3	81·6

nearest number to 71° in the vertical column headed 28·6. This number is 70·8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of the barometer). The substituted number, *i.e.* the true flashing-point of the oil, is 73°.

'Dangerous petroleum' is defined by the Indian Petroleum Act as 'petroleum having its flashing-point below 76° of Fahrenheit's thermometer. Provided that, when all or any of the petroleum on board a ship, or in possession of a dealer, is declared by the master of the ship or the consignee of the cargo, or by the dealer, as the case may be, to be of one uniform quality, the petroleum shall not be deemed to be dangerous if the samples selected from the petroleum have their flashing-points, on an average, at or about 73° of Fahrenheit's thermometer, and if no one of those samples has its flashing-point below 70° of that thermometer.'

The Abel apparatus, with a standard of 22°C., was in 1885 adopted as the legal test in Sweden, and in the year 1888 a Bill was introduced in the Danish legislature to substitute the Abel tester with a standard of 23°C., for the open tester, with a standard of 40°C., then in use in Denmark. In Russia the standard with the Abel-Pensky instrument is 28°C.

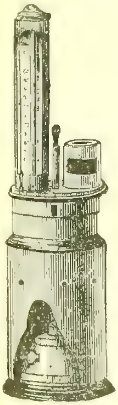

Fig. 11.

The Abel tester is by no means the only form of closed testing apparatus at present in use, and, in addition to those actually employed, a large number of instruments on the closed-cup principle have been devised. Many years ago Tagliabue, of New York, introduced an apparatus (figs. 11 and 12) with a covered brass oil cup communicating by means of a spring valve with a dwarf chimney. The opening of the valve and the simultaneous introduction of a flame into the chimney determines a current of air through the upper part of the oil-cup which sweeps out the inflammable vapour and brings it into contact with the flame. Tagliabue has also constructed a larger instrument of the same form with a glass oil-cup. The Michigan and Wisconsin States tester has a copper oil cup with a copper cover provided with a small orifice to which the test flame is applied. The present New York State tester, devised by Professor Elliott, has a glass oil-cup of comparatively large size with a convex glass cover. Parrish's naphthometer (fig. 13) is provided with a stationary test flame fed by the oil in the testing cup, and Foster's automatic tester (fig. 14), used in Ohio, is similar in principle. In Millspaugh's closed tester (fig. 15) the oil-cup is of glass and is immersed only to the extent of one-tenth of its depth in the water-bath, with the object, apparently, of preventing the overheating of the surface of the oil. Mann's tester (fig. 16) represents an attempt to reproduce in the testing apparatus the conditions prevailing in an ordinary petroleum lamp, the burner of the lamp being replaced by a tube, the stopper of which is blown out when, upon the introduction of a light through a lateral opening, ignition of the vapour occurs. In Pease's closed tester (fig. 17) the vapour is ignited by an electric-spark. The writer remembers seeing, about the year 1870, a closed tester, with electric-spark igniting arrangement, in use by the late Dr. Letheby in his laboratory at the London Hospital. The oil-cup was of glass, with a hinged metal cover, which was blown open when the vapour ignited. In 1882,

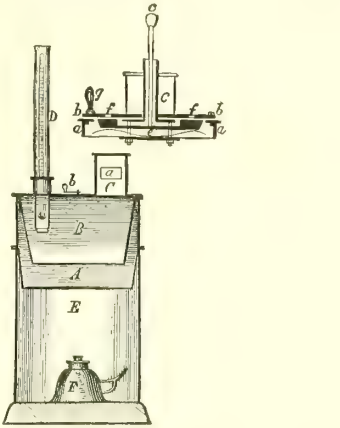

Fig. 12.

The smaller illustration represents in section the cover of the instrument shown in fig. 11. *a*, *a*. Cover. *b*, *b*. Movable bar, with openings *f*, *f*, closed by the bar *e*, beneath which is a spring. *c*. Rod to depress the bar *e*, and thus uncover the openings *f*, *f*. *g*. Handle to move the bar *b*, *b*. C. Hood with opening for insertion of flame.

The larger illustration represents in section a simpler form of the instrument. A. Water-bath. B. Oil-cup. C. Hood, with opening *a*. D. Thermometer. E. Lamp furnace. F. Lamp. *b*. Pivoted cover, closing orifice beneath it.

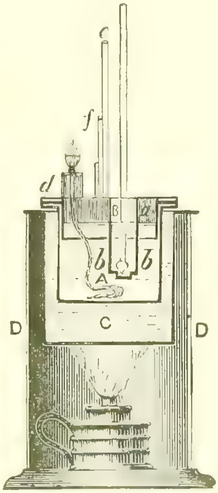

Fig. 13.

A. Oil-cup. C. Water-bath. D. Lamp-furnace. *e*. Screen, with glass plate *f*. B. Chamber communicating with the air, with openings *a* (for circulation of air) and *b*, *b* (to allow passage of oil from B into A). *d*. Cylinder supporting a small wick for test-flame.

Braun, of Berlin, patented a magnetic pendulum arrangement for applying the test flame in the Abel apparatus. In 1881 Engler and Haas made a number of experiments with the Abel apparatus and other testing instruments, and expressed the opinion that the addition of an arrangement for agitating the oil was desirable; Victor Meyer, however, previously proposed the addition of a stirrer. Owing to the facts that in the use of the Abel tester a layer of vapour of gradually increasing thickness is formed upon the surface of the oil and that the temperature of the oil is not uniform throughout, it is, no doubt, necessary that the dimensions of the air space above the oil, the depth to which the test-flame is inserted, the size of the test-flame, the size of the orifices in the cover, the position of the thermometer bulb, and other particulars, should be defined with greater accuracy than would probably be necessary if a stirrer were added, but experience has shown that the Abel apparatus can be readily standardised, and any number of instruments can thus be constructed to give concordant results if used with a reasonable amount of care. The apparatus known as the Engler tester (fig. 18) consists of a copper water-bath surmounted by a second water-bath of glass supporting a glass oil-cup with brass cover in which are two semi-circular openings with hinged lids. Two insulated wires in connection with a small induction coil terminate in platinum points 1 mm. apart at a distance of $\frac{1}{2}$ to $\frac{2}{3}$ cm. from the surface of the oil, and in the centre of the oil-cup is a paddle stirrer attached to a spindle passing through the cover. Beneath the lower water-bath a spirit lamp is placed, and, as the temperature approaches the flashing-point of the oil, the spark is passed at each degree rise in the thermometer, care being taken that the passage of the spark is continued from half to one second. After each application of the spark the oil is gently agitated by rotating the stirrer. When the ignition of vapour occurs the hinged flaps are thrown open. It is claimed that by the use of the double water-bath and the stirrer the heating is rendered slow and regular, and as far as possible independent of the size of the heating flame; also that by the employment of the electric spark, the size, intensity, and distance of the igniting agent from the oil are rendered uniform. Moreover, that the extraneous formation of vapour through the heating of the surface of the oil which may take place when an ordinary test-flame is employed cannot occur in the use of the electric spark as described. Finally it is contended that the conditions prevailing in a petroleum lamp are reproduced to a large extent in the Engler Tester.

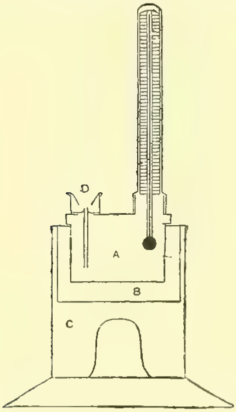

FIG. 14.

A. Oil-cup. B. Water-bath. C. Jacket. D. Flash-jet.

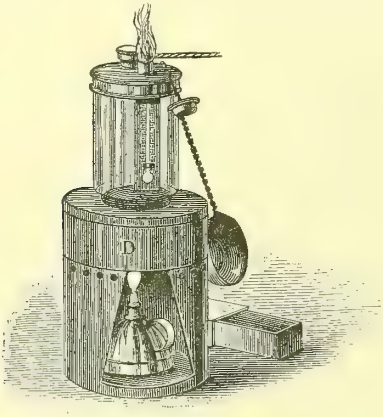

FIG. 15.

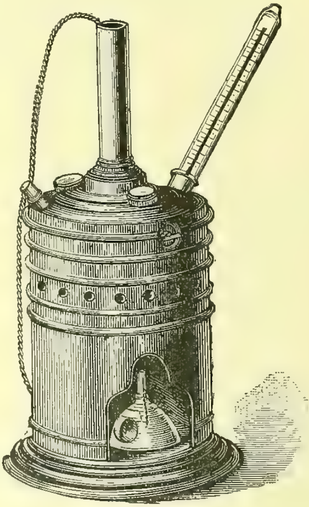

FIG. 16.

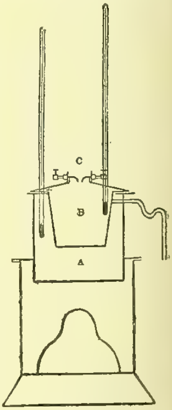

FIG. 17.

A. Water-bath. B. Oil-cup. C. Spark wires.

Among other systems of testing are those of Liebermann, Beilstein, and Stoddard, which are based upon the principle of blowing air at intervals through a jet plunged beneath the surface of the oil, contained in a vessel in which it can be gradually heated, until inflammable vapour is evolved. In Bernstein's tester (fig. 19) the level of the oil is raised from time to time, as the temperature of the oil increases, until vapour issues from the oil chamber and ignites at a stationary flame, and in the Ehrenberg tester a syringe is employed to expel the vapour from the closed oil chamber and bring it into contact with a flame.

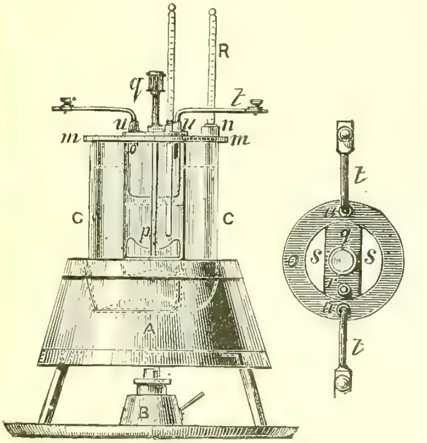

Fig. 18.

A. Copper water-bath. B. Spirit lamp. C, C. Glass water-bath, with filling mark etched upon it. *m*, *m*. Cover. R. Thermometer, supported in the water by collar *n*. *o*. Glass oil-cup, with filling mark. *s*, *s*. Openings with hinged covers. *t*, *t*. Conducting wires, insulated by ebony rings *u*, *u*, and terminating in platinum points. *p*. Stirrer, with handle *q*. *r*. Thermometer in the oil.

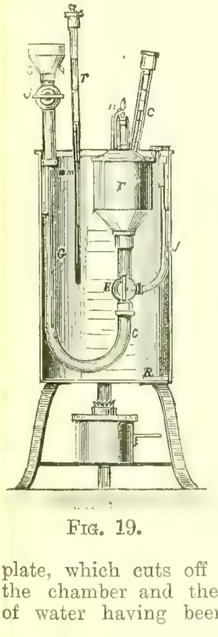

Fig. 19.

There yet remains to be noticed a form of petroleum testing apparatus, employed to some extent in France, in which the flashing-point is deduced from the vapour tension. This apparatus, known as the Salleron-Urbain tester (fig. 20), consists of a closed metallic vessel AA, in the cover of which are inserted a cylindrical chamber B, a regulating screw *r*, a graduated tube *m*, 35 cm. in length, and a thermometer. The cylindrical chamber is closed at the top by a screw-plug *p*, and at the bottom by a sliding plate, which cuts off communication between the chamber and the vessel below. 50 c.c. of water having been placed in the lower vessel, the cylindrical chamber is nearly filled with the petroleum to be tested, the screw-plug replaced, and the apparatus placed in warm water until the temperature has become constant. The water-level in the graduated tube having been adjusted to zero by means of the regulating screw, the oil in the cylindrical chamber is caused to flow out upon the surface of the water in the lower vessel by moving the sliding plate. The expansion of the liberated vapour of the petroleum causes the water to rise in the graduated tube, and, when the level is stationary, its height is read off. In a table published in 1866, Salleron and Urbain give the following figures of sp.gr. and vapour tension of petroleum at 15°C.:

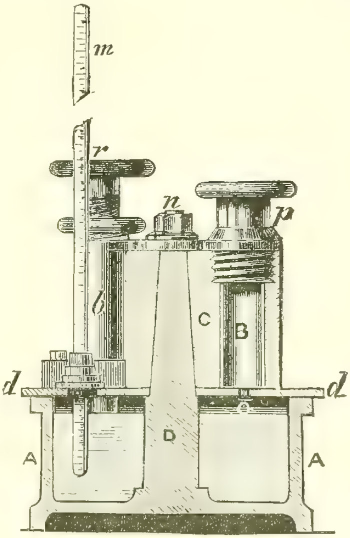

Fig. 20.

Density at 15°C.	Tension in mm. of water	Density at 15°C.	Tension in mm. of water
·812	0	·756	125
·797	5	·735	410
·788	15	·695	930
·772	40	·680	1185
·762	85	·650	2110

In regard to the Salleron-Urbain system of testing, Engler and Haas remark that the method depends upon the assumption that the numbers which express the expansion of the petroleum vapour run parallel with the temperature of the inflammability of all kinds of petroleum; but that the supposition is found not to be correct in all cases, inasmuch as the presence of a small quantity of very volatile hydrocarbons[1] occasions an increased pressure in the apparatus. The general conclusion is, however, expressed that oils which exhibit a tension of not more than 64 mm. of water at 35°C. may be considered safe.

In a report to the New York State Board of Health in 1882, Professor Arthur H. Elliott records the particulars of a large number of experiments with various forms of testing apparatus, and gives the following table of comparative results:—

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[1] Presumably a quantity too small to sensibly affect the inflammability.

Oil used	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	Flashing-points, F.										
No. 1 . .	110°	118°	120°	111°	117°	107°	103°	130°	111°	95°	119°
No. 2 . .	111°	121°	124°	115°	118°	109°	102°	128°	107°	96°	—
No. 3 . .	119°	122°	122°	112°	118°	108°	102°	130°	108°	95°	118°
No. 4 . .	97°	96°	97°	90°	93°	86°	76°	90°	81°	75°	96°

I. Tagliabue (open cup). II. Arnaboldi (open cup). III. Saybolt. IV. Tagliabue (closed cup—small). V. Tagliabue (closed cup—large). VI. Wisconsin State. VII. Abel. VIII. Bernstein. IX. Millspaugh. X. Mann. XI. Foster.

From the statements which have been made, it will be evident that there is a regrettable absence of uniformity in the methods of testing adopted, not only in different countries, but also in the various States of the American Union. The existence of considerable diversity in regard to the test standard to be adopted with any one system of testing is also exhibited in the laws which have been framed in the United States.[1] The latter condition no doubt arises from the fact that, until lately, no systematic attempts were made to determine the relation between the flashing-point of an oil and its safe or dangerous character in ordinary use. Moreover, when petroleum was first introduced, it was often carelessly or improperly handled, and the accidents which occurred led to an exaggerated estimate being formed of the risk involved in the use of the oil as an illuminant, with the result that legislative restrictions of a needlessly stringent description have been placed upon the trade.[1] The experience of many years has conclusively demonstrated that the transport and storage of kerosene of comparatively low flashing-point (say 70°F.—Abel test or its equivalent) and its use in properly constructed lamps is free from risk. This practical conclusion has been confirmed by recent experiments made in this country by Sir Frederick Abel and the writer, and in Germany by the officials of the Standards Office, and it has been found that some oils of high flashing-point may be actually less safe than others of low flashing-point. The tendency of modern petroleum legislation in the United States indicates a recognition of this fact.

(*c*) *Burning quality.*—The testing of the burning quality of kerosene is regularly effected in well-conducted refineries in the United States by burning the oil in lamps of the usual construction and noting the diminution in the size of the flame which occurs in a stated period. The results are, however, dependent upon so many variable conditions that attempts have been made to substitute a test of greater precision; but beyond the improvement of the existing test, the efforts made have not been attended with success. The Saybolt lamp (fig. 21), specially constructed for testing purposes, consists of a tall glass cylindrical graduated reservoir of small diameter, with a burner which furnishes a well-shaped flat flame of considerable height in proportion to the width, a wick carefully selected for the purpose, and a graduated glass chimney. The lamps are burned in water at 60°F., the diminution in the height of the flame and the depression of the oil level being noted.

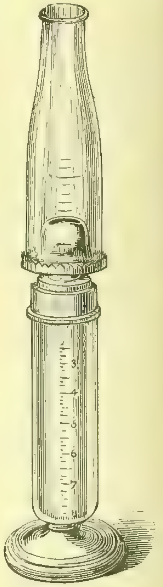

Fig. 21.

In Canada the 'burning percentage' is determined by the use of a lamp thus described:

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[1] In 1886, Colonel Majendie, C.B., Her Majesty's Chief Inspector of Explosives, visited America in company with the writer with the object of obtaining information relative to petroleum legislation in that country. The following particulars (published with Colonel Majendie's permission), relative to the prescribed methods of testing and test standards, are based upon information furnished by H.M. Consul-General and Consuls in the United States, supplemented by information personally collected during the visit referred to.

1. The use of the Tagliabue or other approved instrument is prescribed in the undermentioned States and Cities with the standard fire test specified:

110°F.—States of New York, Pennsylvania, Maryland, and Kansas; Cities of Brooklyn, Syracuse, Newhaven, Richmond, New Orleans, and Philadelphia.

120°F.—States of New Hampshire and Maine; City of Baltimore.

130°F.—State of Arkansas.

150°F.—States of Missouri and Illinois.

2. The use of the Tagliabue (T.), Elliott (E.), or other approved instrument is prescribed in the undermentioned States and Cities, with the standard flashing-point specified:

110°F.—States of Massachusetts (T. open cup), Vermont (T. closed cup), and New Jersey (E. closed cup); City of New York (E. closed cup).

105°F.—State of Iowa (E. closed cup).

110°F.—Cities of Boston (T. open cup), San Francisco (? T. closed cup), Sacramento (? T. closed cup), Los Angeles (? T. closed cup), Milwaukee (? T. closed cup), and Denver (? T. closed cup).

120°F.—States of Ohio, Michigan, Indiana, Wisconsin, and Minnesota.

125°F.—State of Louisiana (? T. open cup).

Note.—In each of the following States a special instrument described in the Act is in use:—Ohio (Foster instrument), Michigan, Indiana, Wisconsin, and Minnesota. In Ohio, the employment of the Foster instrument or an open tester is optional.

3. In the undermentioned States and cities the instrument to be used is not indicated:

110° Fire test.—State of Rhode Island; City of Newark.

110° Flashing-point (open cup).—States of Georgia and Nebraska.

120° Flashing-point (open cup).—State of Tennessee.

125° Fire test.—City of Meriden.

130° Fire test.—State of Kentucky.

[1] In Canada, the use of the Abel tester is prescribed by law, with a minimum standard of 95°F.; but the raising of the test from 73° (the British standard) to 95°F. having been found to involve a loss of 10 p.c., the Ontario refiners in 1886 petitioned for a reduction of the standard.

'The bowl of the lamp is cylindrical, 4 in. in diameter and $2\frac{3}{4}$ in. deep, with a neck placed thereon of such a height that the top of the wick tube is 3 in. above the bowl. A sun hinge burner is used, taking a wick $\frac{7}{8}$ in. wide and $\frac{1}{8}$ in. thick, and a chimney about 8 in. long.' The test is conducted as follows: 'The lamp bowl is filled with the oil and weighed, then lighted and turned up full flame, just below the smoking point, and burned without interference till 12 oz. of the oil is consumed. The quantity consumed during the first hour and the last hour is noted.' The ratio of the two quantities is the measure of the burning quality, and the percentage that the latter quantity is of the former is the 'burning percentage' referred to.

The writer has devoted much time to the perfecting of a system of testing burning quality with lamps of the usual construction, and has succeeded in eliminating some of the sources of discrepancies in the results afforded. Obviously the wick used should be carefully chosen, and, as a fresh wick should be employed for each test, it is important that the wick should be examined before use, and any defective portion rejected. In standardising the wick and verifying its uniformity, the writer has found it advantageous to determine the quantity of a mineral oil of known quality drawn out of a vessel under definite conditions as to temperature &c. by the capillary attraction of a piece of the wick arranged as a syphon (fig. 22). In all cases the wick must be dried immediately before use and immersed in the oil while still warm. The oil chambers of the lamps employed must be of uniform dimensions, and the burners must first be tested to ascertain that they furnish similar flames with the same oil. The wick must be trimmed with scrupulous care before the lamp is lighted, and the oil in the lamp must be maintained at a constant temperature—that of 60°F. being a desirable one. The wick should be raised so as to obtain a flame of the largest size possible without the production of smoke. For recording the size and shape of the flame at the commencement of the experiment and the diminution in size and alteration in shape of the flame at intervals during the progress of the test, the writer has found it convenient to employ a camera by means of which the outline of the flame may be traced on thin paper at intervals (fig. 23). No general agreement has, however, yet been arrived at as to the extent of diminution which shall, under the specified conditions, be permissible with oils to be classed as of satisfactory burning quality. In doubtful cases several tests of the sample should be made, as the results appear to be sometimes affected by causes not well understood. In consequence of the difficulty of devising a thoroughly satisfactory method of testing oils by burning, it has been proposed to establish a distillation test, the inferiority in burning quality being supposed to arise from the oil not being of natural composition or from its containing too large a percentage of the denser hydrocarbons. Attempts in this direction have not, however, been attended with success, oils of different burning quality furnishing in some cases similar results, and oils of equally good burning quality sometimes giving dissimilar results on fractional distillation. The testing of the oil under conditions as nearly as possible approaching to those under which it is practically used appears to be the most rational method of determining the burning quality, and is no doubt the best in the absence of any arbitrary test capable of being easily and expeditiously applied and of furnishing reliable results.

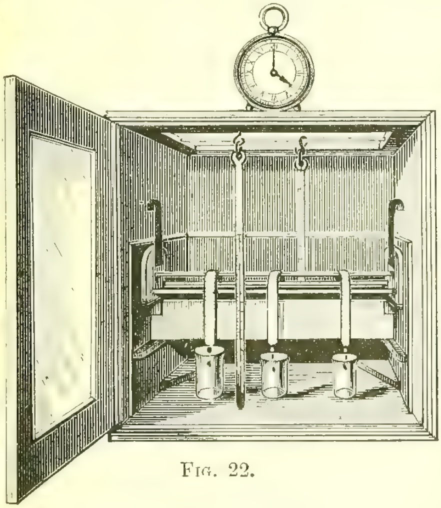

Fig. 22.

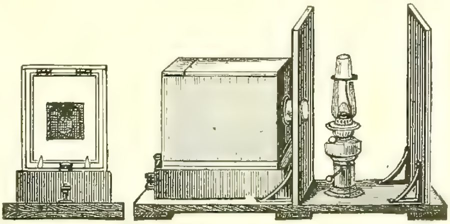

Fig. 23.

Kerosene oil should bear agitation with oil of vitriol without material darkening of colour, and warm water shaken with it should exhibit neither markedly alkaline nor even faintly acid reaction, and should give no precipitate with barium chloride solution. Upon being distilled, kerosene should not evolve sulphurous acid. If the presence of any considerable amount of sulphur compounds is suspected, the oil should be burned in a Referee's gas-testing apparatus and the sulphur products converted into barium sulphate.

4. **Lighthouse oil.** The Trinity House contract conditions for mineral oil intended for use in lighthouse lamps specify that—

(1) The mineral oil required to be supplied under this contract is to be of the best possible quality, the greatest care is to be taken in its preparation, and it must be perfectly free from sulphuric acid.

(2) In all cases, whether the oil be petroleum or paraffin, its flashing-point is to be determined by using the apparatus described in Schedule 1 of the Petroleum Act of 1879.

(3) If the oil be petroleum, its flashing-point is to be not lower than 125° Fahrenheit (close test), and it is to distil between 302° and 572° Fahrenheit, the temperature of the vapour, not that of the liquid, being taken.

(4) If the oil be paraffin, its specific gravity is to be not less than 0·810, nor greater than 0·820, at 60°F.; its flashing-point is to be not lower than 140°F. (close test), and it is to distil between 302° and 572°F., the temperature of the vapour, not that of the liquid, being taken.

(5) The illuminating power of the oil supplied, whether petroleum or paraffin, is to be equal to that of the best colza oil when consumed in a Trinity House Argand lamp.

For the distillation test about 250 grammes of the oil may be taken, the operation being conducted in an ordinary distillation flask with the bulb of the thermometer midway between the shoulder of the flask and the lateral tube leading to the condenser. The upper part of the flask should be wrapped in asbestos cloth.

The United States Lighthouse establishment stipulates that mineral oil supplied for use in lighthouse lamps shall have a specific gravity 'not less than ·802,' a flashing-point of not less than 140°F., and a fire-test of not less than 154°F., both these tests being made with Tagliabue's instrument. The oil is to remain limpid at zero; and 'litmus paper immersed in it for five hours must remain unchanged.' The oil is to be photometrically tested in a fifth-order Hains lamp, and the light is to be equal to that of eighteen sperm candles, and to continue undiminished during five hours' burning.

5. **Lubricating oils.** *a. Colour.* In the case of what are known as pale oils, the trade are accustomed to take exception to any marked increase in the ordinary depth of colour, but as yet there are no accepted standards of colour for these oils, such as have been fixed for kerosene. The writer has, however, for some years past, used the instrument (fig. 24) known as Lovibond's Tintometer[1] in ascertaining and recording the colour of a two-inch column of lubricating oils, and comparative results have thus been furnished for the guidance of the trade.

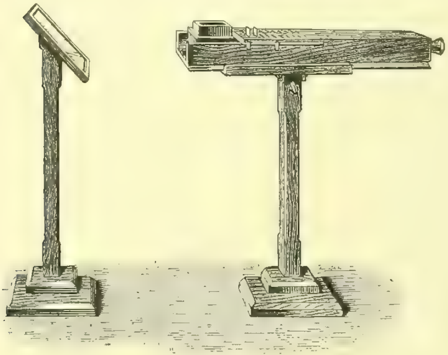

Fig. 24.

b. Odour. Lubricating oils should be free from empyreumatic odour, as the presence of such odour would indicate that the process of refining had not been satisfactorily carried out.

c. Specific gravity. Until recently, mineral lubricating oils of similar description have been graded solely with reference to specific gravity, but, experience having shown that the density is not necessarily an index of the lubricating value, it is becoming generally accepted that the determination of specific gravity is of less importance than that of viscosity.

d. Flashing-point and fire-test. In the determination of the flashing-point by the closed and open tests, and for the determination of the fire test, the writer is accustomed to use an instrument made by Pensky of Berlin. In its closed form this apparatus resembles in principle the Abel tester employed in the examination of kerosene. The water-bath is, however, replaced by an air-bath, consisting of a thick cast-iron vessel which is heated by a Bunsen burner, and the application of the gas test-flame is effected through the medium of a revolving vertical spindle with a non-conducting cap, which can be grasped by the finger and thumb without inconvenience when the apparatus is used at high temperatures. In the use of this instrument the flame of the burner should be

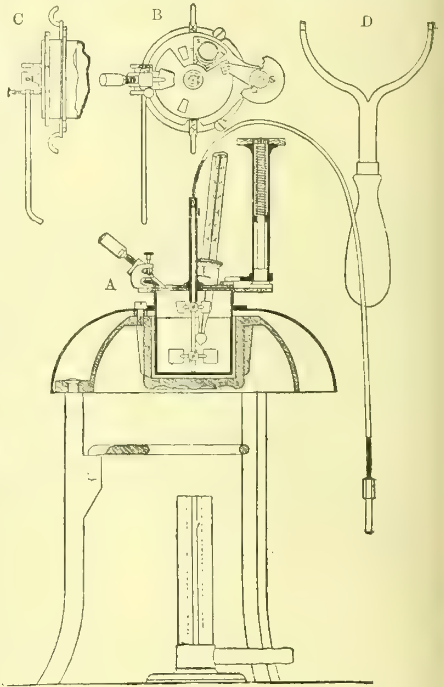

Fig. 25.

A. Apparatus with test-flame in position for igniting the vapour. B. Cover of oil-cup. C. Side view of cover. D. Handle for removing oil-cup from bath when hot.

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[1] This instrument, devised by Mr. Joseph W. Lovibond, of Salisbury, consists of a covered trough or box divided longitudinally by a partition terminating in a vertical knife-edge opposite an eye-piece fixed at one end, and forming two channels slightly diverging from the end at which the eye-piece is placed. In one channel the liquid to be examined, which is contained in a rectangular glass cell, is placed; and in the other channel numbered slips of coloured glass, of known depth of tint, are inserted.

ljusted so that the temperature of the oil rises the rate of about 10°F. per minute. The test form of the apparatus, known as the ensky-Martens tester (fig. 25), is provided with revolving stirrer which agitates the atmosphere oove the oil as well as the oil itself.

If the cover of the oil-cup be removed, the pparatus referred to may be employed for the etermination of the open-vessel flashing-point ıd the fire-test, a gas flame, not more than $\frac{1}{4}$ ch in diameter, being used to produce the nition.

Inspectors of lubricating oils in the United tates commonly use in ascertaining the fire-st an open metallic cup, supported on a tripod and and heated directly by the flame of a pirit lamp, the temperature being raised at the te of eight degrees Fahrenheit per minute.

In some cases it is customary to test the olatility of the oil by noting the loss of weight istained by a given quantity of the oil when kposed for a specified length of time in a shallow essel to an elevated temperature. The oil is ometimes absorbed by filter-paper before ex-posure to heat.[1]

e. Cold-test. The method in which the cold-test' of lubricating oils is made varies ith the description of oil, and to some extent ith the interpretation which the operator places 1 the term. The cold-test of pale oils is sually accepted as being the point at which on gradual reduction in the temperature separa-on of solid hydrocarbons commences. The test ay be conveniently made by slowly cooling the il in a small beaker until it commences to be-ome cloudy, but the result will depend to some ktent upon the length of time occupied in the peration, and upon whether the oil is stirred r not. Some of the more viscous pale oils ontain hydrocarbons which are not very crys-alline, resembling vaseline rather than paraffin ax, and the point at which these hydrocarbons egin to separate under the influence of cold is ot easily determined. In some of such cases is preferable to take the point at which the il becomes reduced to a semi-solid consistency r ceases to flow on inclining the vessel in which is contained. In all cases it is important at the temperature of the bath employed for ooling should not be much lower than that at hich the separation, or solidification, occurs, nd it is therefore desirable to determine ap-roximately the cold-test by a preliminary peration. Where the separation of solid hy-rocarbons is well defined, the test may be made 1 a tube about 1 inch in diameter, containing bout $1\frac{1}{2}$ inch in depth of oil in the following anner: Plunge the tube into a vessel of iced ater, or, if necessary, into ice and salt, until a hin layer of paraffin congeals on the sides, tirring the oil with a thermometer while he reduction of temperature is being effected. 'ake out the tube, wipe it, and holding it be-ween the operator and the window, stir the ontents with a thermometer until the last races of paraffin have disappeared, when the emperature is to be noted. Repeat the experiment, again noting the temperature. Make a third test, and if the results of the last two experiments agree, record this temperature as the cold-test of the sample.

Black oils are tested by cooling them until they cease to flow, as the commencement of the separation of solid hydrocarbons cannot be observed in these oils.

The rules of the New York Produce Exchange provide that the cold-test is to be determined by cooling the sample in a glass vessel, 4 inches in depth and 3 inches in diameter, placed in a refrigerator. A thermometer is to be placed with its bulb in the centre of the oil, and another thermometer is to be placed in the ice-chest outside the oil vessel. If, when the two thermometers both record a specified temperature, the oil is still limpid, the cold-test of the oil is deemed to be satisfactory. Tagliabue has devised a convenient form of apparatus (fig. 26) for the application of this test, the oil-cup being supported on a rocking bar in a jacketed cooling-chamber with a glass window. In practice, however, the cold-test is usually determined by cooling the oil in a glass cylinder $1\frac{3}{8}$ inch in diameter.

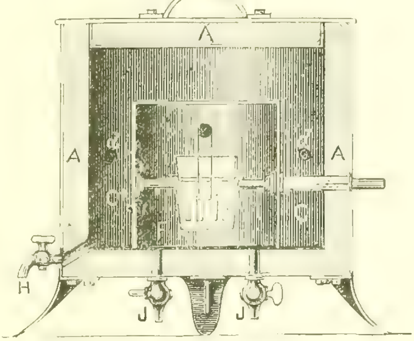

FIG. 26.

A, A, A. Non-conducting jacket. C, C. Ice-chamber. F. Oil-cooling chamber, inclosing the oil-cup, which is supported on a rocking-shaft. H. Tap for draining ice-chamber. J, J. Stop-cocks, through which warm air may be forced when it is desired to raise the temperature in F. *d, d, d.* Thermometers; the central one having its bulb in the oil.

f. Viscosity. It has been already stated that this test is becoming recognised as the proper basis for the grading of lubricating oils, and accordingly its importance is increasing. The test is necessarily an arbitrary one, and there is at present no universally accepted method of testing and expressing the results, though in this country the Redwood viscometer has been adopted by the War Department, the principal railway companies, the Scottish Mineral Oil Association, and the petroleum trade generally. The simplest form of instrument available for the determination of viscosity consists of a glass pipette filled to a mark on the neck and allowed to discharge its contents, the relation between the period occupied in the outflow of a given sample and that required for the discharge of a similar quantity of a standard oil expressing the viscosity of the former sample in terms of the latter. The standardising of glass pipettes is, however, difficult, since the results are affected by the form of the constricted portion of the tube, apart from the size of the orifice, and two pipettes standardised with an oil of a certain viscosity may not afford concordant results with an oil of very different viscosity. Moreover, the maintenance of the required temperature of a sample contained in a glass pipette cannot always be satisfactorily effected. For these reasons the jacketed glass viscometers of Veitch Wilson, MacIvor, and Sacker have not been found to afford sufficiently accurate results.

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[1] The writer is accustomed to expose 25 grammes for 2 hours in a shallow dish to a temperature of 150°F. in the ase of spindle and engine oils, and 250 F. in the case of ylinder oils.

The Saybolt viscometer (fig. 27) is provided with an oil vessel of comparatively large diameter placed in a water-bath of considerable capacity. The viscometer jet is of metal, and is inclosed in a tube extending below the orifice. Immediately above the jet the oil vessel is much contracted in diameter, and a portion is cut away on each side so as to expose an inner glass tube. At a corresponding level, glass windows are inserted in the water-bath. Round the upper part of the oil-vessel is fitted an oil-tight gallery with raised edge, and above the platform of the gallery the oil-cylinder is pierced with a number of small holes. In the use of the apparatus, the bath is filled with water at the required temperature, and, a cork having been inserted in the mouth of the tube inclosing the jet, the oil-vessel is filled with the oil to be tested, until overflow through the orifices referred to occurs. The oil is then stirred with a thermometer, the gallery taking the overflow, and its temperature adjusted if necessary. On withdrawing the thermometer, oil passes from the gallery into the oil vessel to replace that which had overflowed on the insertion of the instrument. The gallery is then emptied by means of a pipette, the length of the oil column being thus determined by the position of the circle of holes; the flow of oil from the jet is started by the withdrawal of the cork from the outer tube; a stop-watch is concurrently set in motion, and the operator, looking through the window in the water-bath and through the glass tube forming the lower part of the oil vessel, stops the watch when the oil-level makes its appearance.

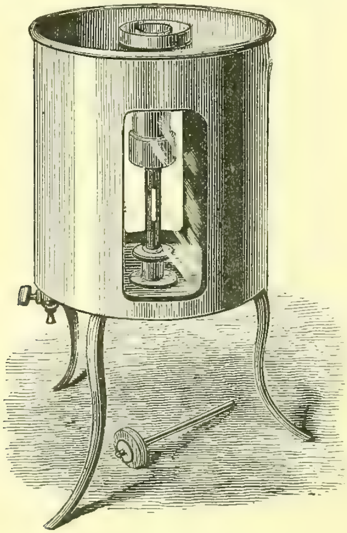

Fig. 27.

The Arvine viscometer for testing cylinder oils consists of a copper tube of small diameter coiled in a bath in which water is kept in a state of ebullition. At its lower end the tube is furnished with a small stop-cock, forming a jet, and at its upper end with a funnel to hold the oil.

The Redwood viscometer (fig. 28) is a modification of the instrument formerly used at the Battersea Works of Price's Patent Candle Company. It consists of a silvered copper oil cylinder, about $1\frac{7}{8}$ inch in diameter and $3\frac{1}{2}$ inches in depth, furnished with an agate jet fitted into a slightly conical metal seating. The cylinder is fixed in a brazed copper water-bath provided with a copper heating-tube projecting at an angle of 45° from the side near the bottom, as well as with a revolving agitator carrying a curved shield to prevent splashing, and a thermometer to indicate the temperature of the liquid in the bath. The oil cylinder has a stopper consisting of a small brass sphere which rests in a hemispherical cavity in the agate jet. The sphere is attached to a wire by means of which it is raised and suspended from a standard which supports a thermometer in the oil. Inside the oil-cylinder, and at a short distance from the top, is fixed a small bracket terminating in an upturned point, which serves as a gauge of the height to which the cylinder is filled. The instrument is supported on a tripod stand. Great care is taken in the construction of the agate jets to secure uniformity, and any slight differences in the rate of flow are corrected by slightly altering the position of the pointed bracket in the oil-cylinder. The instruments (which are made by Messrs. James How & Co., 73 Farringdon Street, E.C., and by Messrs. Townson & Mercer, 89 Bishopsgate Street Within, E.C.) are thus all standardised. The viscometer is used in the following manner:—The bath is filled with a suitable liquid to a height corresponding with the point of the bracket in the oil-cylinder. Water may be used for temperatures up to 200°F., and a heavy mineral oil for higher temperatures. The liquid being at the required temperature, the oil to be tested, which may pre-

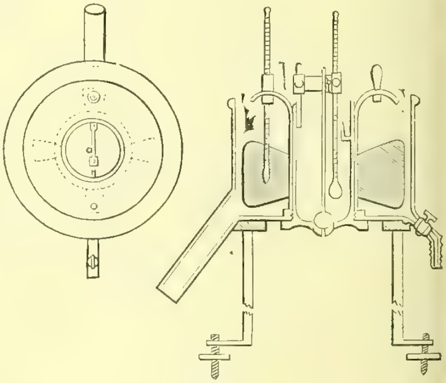

Fig. 28.

viously be brought to the same temperature, is poured into the inner cylinder until its level just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball valve is then raised, a stop-watch at the same time started, and the number of seconds occupied in the outflow of 50 c.c. noted. When oils are being tested at a temperature much above that of the laboratory, a gas flame is applied to the heating tube, and the agitator kept in gentle motion throughout the experiment. The maintenance of the exact required temperature of the oil is thus, after a little practice, rendered easy. It is important that the apparatus should stand perfectly level, and that the oil should be free from dirt, water, or other suspended matter. The writer is accustomed to express the results in terms of the viscosity of rape oil at 60°F., correcting for differences in specific gravity. Accordingly the number of seconds occupied in the outflow of 50 c.c. of the oil under examination is multiplied by 100 and divided by 535 (the average time occupied in the outflow of 50 c.c. of rape oil at 60°F. according to the writer's experiments). The result is then multiplied by the sp.gr. of the oil under examination, at the temperature of the experiment, and divided by 915 (the sp.gr. of refined rape oil at 60°F.).

The Engler viscometer, which is largely used in Germany, is constructed on the same principles as the foregoing, the viscosity of the oil being compared with that of water. Recently this instrument has been improved by the addition of a jacketed air-bath, to maintain a uniform temperature in the outflowing oil.

It will be obvious that, as the length of the column is continuously diminishing during the experiment, the same volume of oil must be allowed to flow out in all cases in order that comparative results may be obtained. To expedite the performance of the test in the case of a very viscous oil, Mr. Alfred H. Allen has fitted to the oil cylinder of the Redwood viscometer an air-tight cap, carrying a tube extending nearly to the bottom of the cylinder, and is in this way enabled to maintain a given head of oil throughout the experiment. The writer has not experienced the need of this modification, but it may be of value in certain cases, since with its adoption the time occupied in the outflow of any given quantity of the liquid, however small, may be compared with the time required for the outflow of a larger or smaller quantity of another oil.

It has been already stated that in expressing the results obtained with the Redwood viscometer a correction is made for differences in sp.gr. As far as the writer is aware, the first published suggestion of an arrangement for eliminating differences due to sp.gr. was made by Prof. W. P. Mason, of Troy, N.Y., who described in the C. N. for Oct. 31, 1884, an apparatus for determining viscosity, and proposed that the length of the column of the oil to be tested should be so adjusted as to be inversely proportional to the sp.gr., and maintained at this calculated length during the outflow of the standard quantity. Mr. Napier, of Glasgow, appears, however, to have previously suggested the reduction of the observed viscosity of an oil to a standard density. In the instrument proposed by Mr. Napier the oil cylinder was in two parts, connected by a flexible tube, the upper part being supported in such a manner that it could be placed at a given point on a fixed scale, the height being determined by the sp.gr. of the oil. The movable part of the oil vessel was provided with an overflow pipe, and by the use of a reservoir with a stopcock it was intended to produce a continuous slight overflow, so that the oil-level should be maintained at a fixed point.

The Mason viscometer was thus described :—

'A glass cylinder 22 inches (55·9 cm.) long, $1\frac{1}{4}$ inches (3·18 cm.) diameter, has a brass lower head $\frac{1}{8}$ inch (0·318 cm.) thick. An orifice is bored in the centre $\frac{1}{32}$ inch (0·794 cm.) in diameter, with bevelled edges, chamfered back $\frac{1}{2}$ inch (1·27 cm.), thus producing a sharp-edged orifice. A line marking the 18-inch (45·72 cm.) level is cut with several finer lines above and below, $\frac{1}{8}$ inch (0·318 cm.) apart, ranging from 16 to 21 inches (40·64–53·34 cm.) above the orifice. The standard temperature is usually 60°F. (15·5°C.). A total flow of 6·103 cubic inches (100 c.c.) is recorded by adjusting the supply so that the head shall be as nearly as possible equal to 18 inches (45·72 cm.) of water, determining this head by calculation from the sp.gr. of the oil. The rule for obtaining the viscosity is to note the time required to discharge the 100 c.c. (6·103 cubic inches) and divide this time by that required where water under a head of 18 inches (45·72 cm.) is used. This ratio is the measure of the viscosity.'

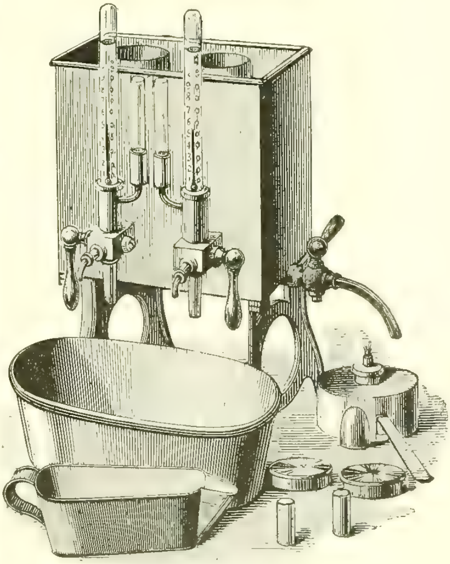

Fig. 29.

In the Barbet viscometer the oil under examination is caused to flow through an annular space formed by fixing an iron rod 4 mm. in diameter precisely in the centre of a brass tube 5 mm. in internal diameter. Increased resistance to the flow of the liquid is thus created, and the apparatus is stated to be more sensitive than an ordinary jet viscometer.

Lepenau's 'leptometer' (fig. 29) consists of two similar metallic cylinders placed vertically side by side in a water-bath, and provided with three pairs of interchangeable jets to be inserted in the stopcocks at the bases of the cylinders. A standard oil having been placed in one cylinder, and the oil to be tested in the other, a pair of jets delivering the oil in drops is selected, and the number of drops falling from the two cylinders between two coincidences of dropping is noted. With dissimilar oils, however, the number of drops is not necessarily a measure of the quantity flowing through the jet, since the size of the drop varies with the nature of the oil.

McNaught's instrument for testing oils consists of two discs, the lower one provided with a raised edge and attached to a vertical spindle revolving in bearings; the upper one resting on a pivot. The space between the two discs having been filled with the oil to be tested, the lower disc is caused to revolve at a given speed. The upper disc is prevented from partaking of the motion of the lower disc, communicated through the oil, by a projecting pin which comes into contact with a pendulum; the extent to which the pendulum is removed from the perpendicular being the measure of the viscosity of the oil.

The paddle viscometers of Napier of Glasgow and Cockerell of Manchester are based upon the principle of taking the speed of a paddle-wheel revolving in the oil as a measure of the viscosity. A series of concentric rings, on a vertical axis, revolving in concentric annular spaces (figs. 30 and 31), and a hollow vertical drum revolving in a cylinder of slightly greater diameter containing the oil have also been employed by Mr. Napier. The use of a pendulum oscillating in the oil has besides been proposed. Another method of estimating viscosity which has been proposed is to note the length of time occupied in the ascent of a bubble of air through a given column of liquid, and Professor Mills has carried out this idea by using hollow glass bulbs, but without obtaining promising results.

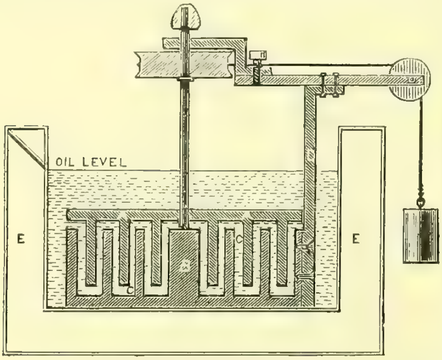

FIG. 30.—Section.

A, A, A. Concentric rings, $\frac{1}{10}$ in. thick, $\frac{3}{4}$ in. deep. B, B, B Ditto. C, C. Spaces of $\frac{1}{10}$ in. between fixed and moving rings. D. Support for driving gear. E, E. Jacket.

g. Lubricating property by direct mechanical tests. Machines have been devised by Thurston, Woodbury, Ingram and Stapfer, and others, for the mechanical testing of lubricating value. These machines are provided with accurately fitting frictional surfaces, between which the oil to be tested is placed, the heat and resistance at given speeds being determined. It cannot be said, however, that results of much practical utility in determining the value of lubricating oils have thus been obtained. Experience has, in fact, demonstrated that in any machine for the mechanical testing of such oils, the conditions under which the lubricants are to be actually employed must be reproduced. The writer has, therefore, been led to the conclusion that the viscosity of a mineral lubricating oil affords the best guide to its lubricating value, the consumer being thus enabled to select from time to time oils similar to those which he has found by practical experience to afford the best results under the particular circumstances of his case. This branch of the subject has been treated in some detail in a paper by the writer, published in the 'Journal of the Society of Chemical Industry,' vol. v. (1886), p. 121.

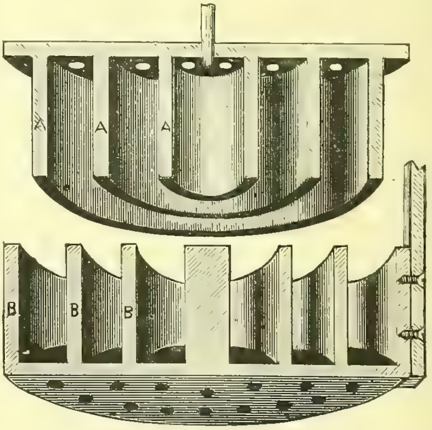

FIG. 31.—Perspective section.

h. Purity. In the examination of mineral lubricating oils it is sometimes necessary to apply chemical tests. Oils intended for the lubrication of steam-engine cylinders should be pure hydrocarbons, saponifiable oils being liable to decomposition by the high-pressure steam, and the liberated fatty acids forming metallic soaps. The percentage of saponifiable oils present may be readily determined by treatment with alcoholic potash and extraction from the aqueous solution of the soap with ether. When a mineral lubricating oil is boiled with water and the liquids allowed to separate, the water should retain its transparency, and should exhibit no acid or alkaline reaction. Occasionally mineral lubricating oils are adulterated with resin oil, and their viscosity is increased by the addition of aluminium palmitate or oleate, or of india-rubber. If the presence of any of these adulterants is suspected the methods of examination described in Allen's 'Commercial Organic Analysis,' vol. ii., may be employed.

6. **Paraffin.** *a. Melting-point.* The so-called melting-point of paraffin is understood in the trade to be the temperature at which the melted material begins to solidify. The two methods chiefly adopted in determining this point are known respectively as the English test and the American test. The English test is conducted by melting the paraffin in a test-tube about $\frac{3}{4}$ in. in diameter, and stirring the fluid material with a thermometer while the tube is held in the air until in the process of cooling a point is reached at which the crystallisation of the hydrocarbons liberates enough heat to arrest the reduction of temperature, and the mercury remains stationary for a short time. Mr. Saybolt has devised a convenient form of apparatus for applying this test simultaneously to several samples, the melted material being contained in a series of parallel troughs mounted on a carriage so as to travel backwards and forwards, the thermometers being held rigidly above the troughs in a frame in such a position that the bulbs are just immersed. The American test is made by melting enough of the material to three-parts fill a hemispherical dish about $3\frac{3}{4}$ in. in diameter, allowing the paraffin to cool in the air and noting the temperature at which a very thin film extends from the sides of the vessel to a thermometer with a round bulb half an inch in diameter suspended in the centre of the dish so that the bulb is only three-fourths immersed. The melting-point by the American test is usually from $2\frac{1}{2}$–3°F. higher than that indicated by the English test. Some operators prefer to note the temperature at which a minute quantity of the sample, previously fused into a capillary tube (care being taken not to overheat the material), becomes solidified when the tube is allowed to cool slowly by the side of a sensitive thermometer in a beaker of water.

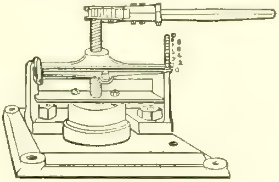
FIG. 32.

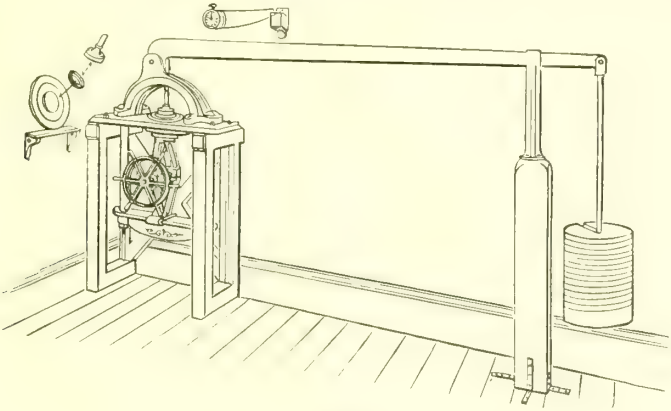
FIG. 33.

b. Percentage of oil. The determination of the percentage of oil in paraffin scale is a purely arbitrary test, as there is no natural line of demarkation between the solid and liquid hydrocarbons of petroleum. The test is made by subjecting the material to pressure and noting the loss in weight, but the results obtained depend upon the temperature at which the operation is conducted, the quantity of material in relation to the diameter of the press-cake and the amount and duration of pressure. The writer had some years ago a press (fig. 32) constructed for the purpose with a steel crosshead, the deflection of which was magnified by levers, and the amount of pressure applied was thus indicated, and he now makes use of a press (fig. 33) wherein a heavily weighted lever is used to regulate the pressure. Both these presses are provided with circular press-cups and plungers $5\frac{5}{8}$ in. in diameter, and the pressure employed in testing American paraffin scale is 9 tons on the total surface. The quantity of material operated upon is 500 grains, and the pressure is applied for five minutes at a temperature of 60°F. The paraffin is placed between circular pieces of calico cut with a steel punch to fit the press-cup, and the oil expressed is absorbed by a sufficient number of discs of blotting-paper placed above and below the cloth containing the cake. The temperature of the press-cup and the plunger is indicated by thermometers inserted in mercury-cups, and the paraffin is also brought to the standard temperature before being pressed. The testing press designed by Mr. McCutchon (figs. 34 and 35) is furnished with a helical steel spring, the extent of compression of which indicates the amount of pressure applied. Messrs. Clarkson and Beckitt, of Glasgow, have made an excellent hydraulic press (fig. 36) for the purpose, which occupies less space than a lever press.

c. Percentage of water and dirt. The percentage of water in paraffin scale may be determined by heating a weighed quantity in an evaporating dish to a temperature somewhat above the boiling-point of water, the melted paraffin being continuously stirred until the whole of the water has been driven off, when the loss in weight is noted. If the quantity of water present is large the percentage may be determined by distillation or by subsidence, the paraffin being retained in a melted state until the water has separated. Mr. Sutherland[1] has introduced a convenient form of apparatus for making the latter test, consisting of a bulbed tube (taking a charge of 50 grms. of paraffin) the lower part of which is graduated. In the use of this instrument the greater portion of the melted paraffin may be readily poured off by removing the tube from the heating bath when the water has separated, and plunging the lower end into cold water so as to seal the water by causing the solidification of a layer of paraffin above it. The operation may then be completed by dissolving the remaining paraffin in warm petroleum spirit (hydrated). In this method of testing, the dirt is usually estimated with the water, but if the proportion of dirt is considerable it should be collected on a filter paper, washed with mineral spirit, dried and weighed.

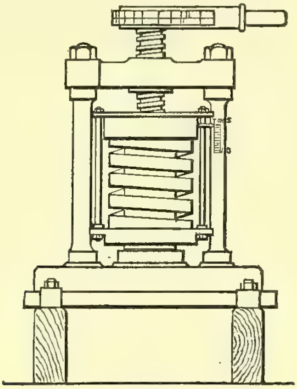

Fig. 34.

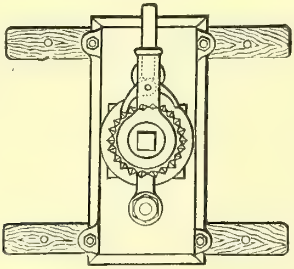

Fig. 35.

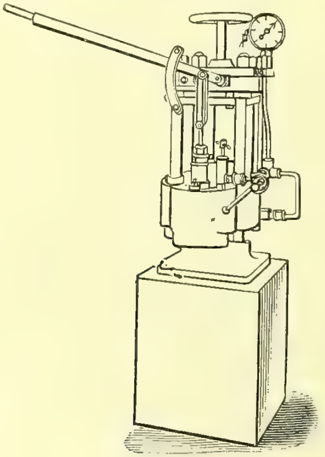

Fig. 36.

The following methods of testing Scotch paraffin scale and heavy mineral oils have been recently agreed upon by the chief chemists of the Scottish Mineral Oil Association, Price's Patent Candle Company, and the writer.

I. *Scale analysis.*

1. *Sampling of hard scale.* The sample is to be taken by means of a metal tube, which is made slightly conical; the small end is inserted in the scale, and by means of a handle, which is removable, it is forced through the scale to be sampled. By this means a cylindrical core of paraffin is obtained.

Care must be taken to see that the tube is of such a length that the sample will represent the whole length or depth of the cask, waggon, or bing.

2. *Preservation of samples of scale.* Immediately after the sample has been drawn it is to be thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The bottles are then finally sealed in the usual manner. The scale should be tightly packed into the bottles, which should be completely filled.

3. *Determination of oil in scale.* (a) *Press to be used.* While no one special form of press is recommended for general adoption, the press used must have some arrangement for indicating the pressure applied. The cup in which the scale is placed during the application of pressure to have an area of 20 square inches.

(b) *Preparation of the sample.* A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is to be allowed to cool over night to a temperature of 60°F. The solid mass is then ground to a fine powder, a portion of which is used in the determination of the oil.

(c) *Quantity of scale to be used.* The quantity of scale to be used in the determination of oil is to be 250 grains, which quantity may, however, be reduced to 150 grains in the event of the scale containing much oil (over 7 p.c.). With 'soft' scale the smaller quantity should be taken.

(d) *Temperature at which the scale is to be pressed.* The temperature of the scale and the press is to be 60°F.

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[1] Journ. Soc. Chem. Ind., vol. vi. (1887) p. 123.

(e) *Time which the scale is to remain under pressure.* The scale is to remain under pressure for fifteen minutes.

(f) *Pressing cloths and papers.* Fine linen pressing cloths and a number of layers of filter-paper, sufficient to absorb all the oil, to be used. The exterior papers must not be soiled by oil.

(g) *Pressure to be applied.* The maximum pressure is to be 10 cwt. per square inch, and the working pressure 9 cwt. per square inch.

4. *Determination of water in scale.* The amount of water present in scale may be determined by either of the following processes:

(a) *Distillation from a copper flask.* From 1 to 2 lbs. of the scale are heated in a conical copper flask of about the dimensions shown in the annexed sketch; this is connected to an ordinary Liebig condenser. By means of a powerful Bunsen burner or lamp, the water, accompanied by a small quantity of light oil, is volatilised and condensed. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this is to be washed out with hydrated gasoline or naphtha and added to the principal quantity.

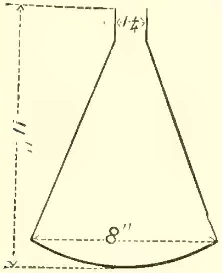


Fig. 37.

(b) *Price's Company's method.* 500 grains of the scale to be tested are weighed in a tared porcelain basin and heated with constant stirring to 230°F. until bubbles cease to be given off; the loss is then determined.

500 grains of the same scale, which has been freed of its water and dirt by melting at a gentle heat and subsidence, are to be heated in the same way, to a similar temperature, for the same time, and the loss again determined. The loss in the second instance is now to be deducted from the loss found in the first experiment, and the remainder is then to be taken as the quantity of water present.

5. *Determination of dirt in scale.* The amount of dirt present in scale is to be determined by melting a weighed quantity of the scale and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha, thrown on a weighed dry filter-paper, washed with naphtha or gasoline, dried and weighed. When available, the quantity of scale to be used in the determination of the percentage of dirt should not be less than 7,000 grains.

6. *Calculation of the results of the analysis of scale.* As the oil is determined on scale which has been freed from water and dirt, the result must be calculated back to the original scale containing water and dirt.

7. *Determination of the melting (setting) point of solid paraffin.* This is to be determined by what is known as the 'English' test *i.e.*, a test tube about 1 inch in diameter is filled to the depth of about 2 inches with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point.

II. *Flashing-point of heavy mineral oil.*

8. *Determination of the flashing-point of heavy mineral oil.* The oil cup and cover of the ordinary 'Abel' flash-point apparatus are to be employed. The cup is filled with oil in the usual manner, and the rate of heating is to be such that at least fifteen minutes are taken in raising the temperature of the oil to 300°F. In the event, however, of a dispute arising as to the correct flashing-point of a heavy mineral oil, the question is to be decided by means of the 'Pensky-Marten's' apparatus (S. C. I. 8, 734).

III. *Viscosity of mineral oil.*

9. *Determination of the viscosity of mineral oil.* The instrument known as the 'Redwood' viscometer is that which is to be employed in the determination of the viscosity of mineral oils. The instrument is to be standardised according to the directions given by Mr. Boverton Redwood (S. C. I. 5, 127). Ordinary results are to be expressed, as the time in seconds which 50 c.c. of the oil take to flow through the orifice at a temperature of 70°F.

IV. *Setting-point of mineral oil.*

10. *Determination of the setting-point of mineral oil.* This is determined in the following manner. Into a test tube having a diameter of about 1¼ inches the oil to be tested is added to the depth of about 2 inches; the tube is then immersed in a freezing mixture, the oil being slowly stirred with a thermometer till it is cooled down considerably below the temperature at which solid paraffin first appears. The tube is then removed from the freezing mixture, the oil constantly stirred with the thermometer, and the point carefully watched at which the last trace of solid paraffin disappears. This operation is repeated with the same sample of oil until two experiments give concordant results, the temperature so found being the setting-point.

B. R.

PE-TUN-TSE, PETUNSE, or **PETUNTZE** *v.* China-stone.

PETUNZITE *v.* China-stone.

PEWTER *v.* Tin.

PHÆOSIC ACID *v.* Laurus nobilis.

PHÆOSIN *v.* Laurus nobilis.

PHENACETIN *Para - acetphenetidine* $C_2H_5O.C_6H_4.NH.COCH_3$ is probably prepared by ethylating para-nitrophenol by Kolbe's method (J. pr. [2] 27, 424), reducing the nitrophenetole and acetylating the resulting amidophenetole by boiling with glacial acetic acid.

It crystallises in colourless needles, melts at 132·5°, and is sparingly soluble in water, soluble in glycerol, and readily soluble in alcohol and acetic acid (Hinsberg and Kast, C. C., 1887, 358; Utescher Abstr., S. C. I., 1888, 87). According to Dujardin-Beaumetz (Chem. and Drug., 33, 244), para-acetphenetidine, if toxic, is only so in slight degree. It is a safe and trustworthy antipyretic, entirely free from injurious secondary effects, and in doses of 0·2 to 0·5 gram produces a gradual lowering of temperature during 4 to 6 hours, when a maximum depression of 2°C. is reached (D.-B.; H. and K.; U.; Ghillany, Abstr. S. C. I., 1887, 676; Kobler, C. C., 1887, 1092; Hoppe, *ib.*, 1888, 609; Rumpf, *ib.*, 1888, 1103). In larger doses (1 to 2 grams) it acts as an antineuralgic.

Phenacetin, owing to its high price, may be adulterated with acetanilide (antifebrine), but this may be detected by heating with aqueous soda and chloroform, whereby the characteristic odour of phenyl isonitrile (carbamine) is liberated; phenacetin under these conditions does not yield the isonitrile, and may be recognised, inasmuch as chlorine water or an aqueous solution of bleaching powder colours its aqueous solution reddish-violet, afterwards changing to red, whilst an aqueous solution of potassium permanganate produces with it a violet colour, which eventually changes to ruby-red (Schwarz, C. C., 1888, 1010; Ritsert, *ib.*, 1069).

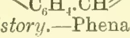
PHENACITE *v.* BERYLLIUM.

PHENANTHRANAPHTHAZINE *v.* AZINES.

PHENANTHRAQUINONE *v.* PHENANTHRENE.

PHENANTHRAQUINONE RED *v.* HYDRAZONE COLOURING MATTERS.

PHENANTHRENE *Orthodiphenylene-ethylene*



$\left\langle\begin{matrix}C_6H_4.CH\\C_6H_4.CH\end{matrix}\right\rangle$ (*cf.* Schultz, A. 196, 1).

History.—Phenanthrene seems to have been discovered almost simultaneously, in 1872 by Fittig and Ostermayer (B. 5, 933; A. 166, 361), Graebe and Glaser (B. 5, 861, 968, 982; A. 167, 131), and by Limpricht and Hayduck (B. 6, 532; A. 167, 177).

Formation and Occurrence.—Phenanthrene forms the chief constituent of the solid, readily-soluble portions of crude anthracene. It is obtained with other hydrocarbons when vapours of toluene (Graebe, B. 7, 48), stilbene, dibenzyl (Graebe, A. 167, 157; Barbier, A. Ch. [5] 7, 532), turpentine (Schultz, B. 10, 113), or Baku petroleum residues (Letny, B. 11, 1211), or mixtures of diphenyl and ethylene, benzene and styrene, or benzene and ethylene (Barbier, *l.c.*), are passed through a red-hot tube, and is a constituent of a product obtained during the distillation of Idrian quicksilver ores (Goldschmiedt, B. 10, 2022). It is also present in the product obtained when morphine or codeine are distilled with zinc-dust (Gerichten and Schrötter, A. 210, 396; B. 15, 1484, 2179). Synthetically it has been prepared by the action of sodium on orthobromobenzyl bromide (Jackson and White, Am. 2, 391).

Preparation.—The raw material for the production of phenanthrene is that portion of crude anthracene readily soluble in petroleum spirit or benzene. If not free from high boiling phenols or from acridine it is extracted, in the first instance, with aqueous caustic soda or sulphuric acid. The residue is then fractionated, and the fraction boiling at 320–350° submitted to fractionation between 339–342° (Schmidt, B. 12, 1159). The product, which still contains some anthracene and other hydrocarbons, is crystallised from a considerable bulk of alcohol, and the phenanthrene which remains in the mother-liquors purified by crystallisation. As phenanthrene is less readily oxidised than anthracene, purification can also be effected by oxidising the impure material with potassium bichromate and dilute sulphuric acid (Anschütz and Schultz, A. 196, 35), and crude anthraquinone prepared from crude anthracene serves as a convenient source of the hydrocarbon, since the phenanthrene can be separated by extraction with and crystallisation from 85 p.c. alcohol (*cf.* Schmidt, J. pr. [2] 9, 256). Wense (B. 19, 761, footnote) states that phenanthrene can be readily purified by dissolution in toluene. Three parts of the crude material are dissolved in five parts of toluene, the solution cooled to 10°, and the crystalline separation, consisting largely of anthracene, filtered off. The residue left after removal of the solvent by distillation is again treated in the same way, and the phenanthrene contained in the mother-liquor further purified by fractional distillation, and subsequent crystallisation from 70 p.c. alcohol.

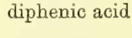
On the laboratory scale, phenanthrene is conveniently purified by conversion in alcoholic solution into the picrate (m.p. = 143–145°), which crystallises from the solution in golden-yellow needles, and yields the pure hydrocarbon on treatment with ammonia (Limpricht, B. 6, 532; *cf.* Hayduck, *l.c.*).

Properties.—It crystallises in white scales, melts at 100°, boils at 340° (therm. in vapour), and is insoluble in water, readily soluble in hot alcohol, ether, carbon bisulphide, acetic acid and benzene, forming solutions which exhibit a pale-blue fluorescence. 100 parts of toluene dissolve 33·02 parts at 16·5°, and 100 parts of absolute alcohol dissolve 2·62 parts at 16° and 10·08 parts at 78° (Bechi, B. 12, 1978), whilst 100 parts of 95 p.c. alcohol dissolve about 2 parts at 13–14° (Graebe, A. 167, 136).

Reactions.—Oxidising agents convert phenanthrene into *phenanthraquinone*, and eventually into *diphenic acid*. Sulphuric acid dissolves it with the formation of two isomeric *monosulphonic acids* (Graebe, A. 167, 152; Japp, C. J. 37, 83), and nitric acid converts it into a mixture of three isomeric *mononitrophenanthrenes* (Schmidt, B. 12, 1154). With chlorine and bromine it forms unstable addition compounds, which very readily undergo conversion into halogen derivatives (Fittig and Ostermayer, *l.c.*; Hayduck, *l.c.*; Zetter, B. 11, 165).

Of the various phenanthrene derivatives, phenanthraquinone and diphenic acid will alone be described here.

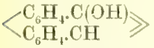
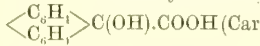
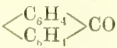
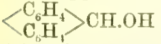
Phenanthraquinone



$\left\langle\begin{matrix}C_6H_4.CO\\C_6H_4.CO\end{matrix}\right\rangle$.

Preparation.—The portion of the easily-soluble solid constituents of the coal-tar fraction boiling at 320–340°, preferably free from high-boiling phenols and acridine, is oxidised in quantities of 100 grms., each amount being added to a warm solution of 300 grms. of potassium bichromate in 900 grms. of sulphuric acid diluted with 1·5 litres of water contained in a large porcelain dish. The reaction is at first very vigorous, but afterwards requires to be assisted by gentle warming, a further 300 grms. of powdered potassium bichromate being added, and the liquid finally boiled for some time. After cooling, the reddish-yellow insoluble quinone is filtered off through linen and washed with water until the runnings are no longer coloured. The product, which consists of phenanthraquinone mixed with some phenanthrene, anthraquinone, diphenic acid, diphenyleneketone, carbazole, and acridine, is dried, powdered, stirred into concentrated sulphuric acid, and after 24 hours mixed with water, heated to boiling, and filtered with the object of removing chromium salts, diphenic acid, acridine, &c., the last traces of organic acids or hydrocarbons being removed by extracting the residue with very dilute, cold aqueous caustic soda, washing with water, drying, and extracting with ether. The residue, consisting of phenanthraquinone and anthraquinone, is freed from the latter by digestion with warm, concentrated aqueous sodium bisulphite in which the phenanthraquinone dissolves, and from which, after filtration, it is precipitated by addition of a solution of potassium bichromate in dilute sulphuric acid. After washing with water and drying, the phenanthraquinone is crystallised from alcohol or coal-tar hydrocarbons (Anschütz and Schultz, A. 196, 38).

Properties.—It crystallises in tufts of long orange-yellow needles, melts at 198° (Fittig and Ostermayer, *l.c.*), 200° (Schmidt, J. pr. [2] 9, 255), 202° (Hayduck, *l.c.*), 205° (Graebe, *l.c.*), boils above 360° without decomposition, sublimes in orange-red tables, and is very slightly soluble in water, soluble in alcohol and ether, and readily soluble in benzene and acetic acid. Concentrated sulphuric acid dissolves it in the cold forming a green-coloured solution.

Reactions.—Phenanthraquinone, unlike anthraquinone, dissolves in alkaline bisulphite solutions, and is readily reduced to the hydroquinone by warming with sulphurous acid (Graebe, *l.c.*). When boiled with fuming hydriodic acid it is reduced to *phenanthrone*  $\left\langle\begin{matrix}C_6H_4.C(OH)\\C_6H_4.CH\end{matrix}\right\rangle\!\!\rangle$ (Japp and Klingemann, C. J. Proc. 1890, 31); when distilled with zinc-dust it yields phenanthrene. On nitration with boiling nitric acid it forms *mononitrophenanthraquinone* (Anschütz and Schultz, B. 9, 1404), and with a mixture of concentrated nitric and sulphuric acids two isomeric *dinitro-* derivatives, of which that melting at 294° is the chief product (Graebe, *l.c.*). Towards alkalis, phenanthraquinone exhibits a remarkable behaviour; thus, when boiled with aqueous caustic potash, soda, or baryta it is converted initially into *diphenylglycollic acid*  $\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle C(OH).COOH$ (Caro, B. 10, 126, 534), which by further action of the alkalis yields *diphenyleneketone*,  $\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CO$ (Anschütz and Japp, B. 11, 211), and *fluorene alcohol*  $\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH.OH$ (Anschütz and Schultz, A. 196, 47); when boiled with alcoholic potash it gives *diphenic acid* (Anschütz and Schultz, A. 196, 49), and when distilled with soda-lime it yields *diphenyl* (Graebe, *l.c.*), and with caustic lime *diphenyleneketone*, *fluorene alcohol*, and *fluorene* (Anschütz and Schultz, A. 196, 44).

Phenanthraquinone yields condensation compounds with many substances; those with the sulphonic acids of aromatic hydrazines are orange and red dyes (*cf.* Actieng. für Anilinfab., Germ. Pat. 40745 of Jan. 27, 1887; *v.* HYDRAZONE COLOURING MATTERS).

Detection.—Phenanthraquinone in acetic acid solution, on addition of a drop of crude coal-tar toluene (containing thiophen) and some concentrated sulphuric acid, forms a bluish-green liquid, which, when poured into water and shaken out with ether, gives an intense reddish-violet colour to the ethereal solution, an appreciable colouration being obtained when only 0·0005 grm. of the quinone is employed (Laubenheimer, B. 8, 224; V. Meyer, B. 16, 1624, 2972).

Diphenic acid $COOH.C_6H_4.C_6H_4.COOH$.

Preparation.—Phenanthraquinone is heated in a reflux apparatus with a solution of 2 parts of potassium bichromate in 3 parts of sulphuric acid diluted with 5 parts of water; when dissolved the solution is cooled, filtered, and the residue dissolved in ammonia, precipitated by an acid, and the precipitated diphenic acid purified by crystallisation from alcohol (Hummel, A. 193, 116).

Properties.—It crystallises in scales or monoclinic prisms, melts at 228–229° (Schultz, A. 203, 97), sublimes in needles, is tolerably soluble in hot water, and readily soluble in alcohol and ether. Acetic chloride (Anschütz, B. 10, 326) or dehydrating agents such as acetic anhydride (Anschütz, B. 10, 1884) or sulphuric acid (Graebe and Mensching, B. 13, 1302) convert it into the *anhydride*, which by prolonged heating decomposes into carbon dioxide and *diphenyleneketone*.

Orthodiamidodiphenic acid. $COOH.C_6H_3(NH_2).C_6H_3(NH_2).COOH$ [NH_2:COOH = 1:2] is obtained when a mixture of equal weights of orthonitrobenzoic acid, aqueous caustic soda of 40° Bé., and water is heated at 100° with a like amount of zinc-dust added from time to time in small quantities, and the reduction continued until a test after boiling with water gives a colourless solution. The reduced mass is then boiled out with hydrochloric acid, and the filtrate on cooling gives an almost complete separation of the hydrochloride of orthodiamidodiphenic acid, which can be purified by dissolution in ammonia and precipitation with acetic acid (Bad. Anilin- und Sodafabrik, Germ. Pat. 43524 of Oct. 28, 1886; *cf.* Griess, B. 7, 1612).

Properties.—The tetrazo- compound interacts with naphtholsulphonic or naphthylaminesulphonic acids forming red, violet, or blue direct cotton dyes (B. A. S. F., *l.c.*).

Metadiamidodiphenic acid [NH_2:COOH = 1:3] is obtained from metanitrobenzoic acid by the method just given for the ortho- compound (Griess, B. 7, 1609), and from dinitrodiphenic acid (prepared from dinitrophenanthraquinone, m.p. = 294°) by reduction with tin and hydrochloric acid (Struve, B. 10, 76; Schultz, A. 196, 26).

Properties.—It crystallises with $1\frac{1}{2}$ H_2O in short needles sparingly soluble in water and alcohol. The tetrazo- compound interacts with naphthols or naphtholsulphonic acids forming orange, scarlet, or violet disazo- dyes, which are almost destitute of the property of dyeing unmordanted cotton, and hence have no technical value (Paul, Germ. Pat. 41819 of Oct. 5, 1886; Beyer and Kegel, Germ. Pat. 44089 of Feb. 26, 1887; 44161 of June 24, 1887).

Paradiamidodiphenic acid (Strasburger, B. 16, 2347). W. P. W.

PHENETOLE $C_6H_5.O.C_2H_5$.

Preparation.—Phenetole can be obtained by heating potassium phenate with ethyl iodide (Cahours, A. Ch. [3] 27, 463), or by heating a mixture of equal parts of phenol and phosphorus pentoxide at 200° and gradually adding alcohol (Kastropp, B. 10, 1685). It is prepared by heating molecular proportions of crude calcium or sodium sulphovinate and sodium phenate (prepared by mixing molecular proportions of phenol and aqueous caustic soda of sp.gr. = 1·33) at 150° for some hours (Kolbe, J. pr. [2] 27, 424).

Properties.—It is a colourless, aromatic liquid, insoluble in water, but soluble in alcohol and ether. It boils at 172° (Cahours), at 171·5–172·5° at 762·4 mm. (Schiff, A. 220, 105).

PHENETOLE RED *v.* AZO-COLOURING MATTERS.

PHENICIENNE *v.* PHENYL BROWN.

PHENOL AND ITS HOMOLOGUES. The hydroxy- derivatives of benzene and its homologues are usually classed together as phenols, and are distinguished as monohydric, dihydric, &c., according to the number of hydroxyl- radicles present in the molecule.

Occurrence.—Several of the most important monohydric phenols—*e.g.*, phenol, cresols and xylenols—are present in coal tar, blast-furnace tar, coke-oven tar, shale tar and beechwood tar. Other phenols—*e.g.*, thymol, hydroquinone (quinol), orcinol, and phloroglucinol—occur in certain plants, frequently as glucosides. Mono- and di-methyl ethers of pyrocatechol, homopyrocatechol, pyrogallol, methylpyrogallol and propylpyrogallol occur in beechwood tar (*v.* CREOSOTE), and the pyrogallic ethers have been isolated from shale tar.

Preparation.—From the corresponding hydrocarbons phenols can be obtained by direct oxidation with dry oxygen in the presence of aluminium chloride (Friedel and Crafts, Bl. 31, 463). Other synthetical methods, of more or less general application, have been devised, but the processes in use on the large scale are two in number:—

(1) Fusion of the sulphonic acids derived from the hydrocarbons with excess of caustic potash or soda.

(2) Conversion of the amido- derivatives of the hydrocarbons into diazo- compounds, and decomposition of these by boiling with water acidified with sulphuric acid.

General Reactions.—(1) In aqueous solution many phenols give characteristic colourations—green, blue, violet, &c.—on treatment with neutral ferric chloride. The reaction is dependent upon the presence of hydroxylic hydrogen, since no colouration is obtained when this has been displaced by alkyl or acid radicles.

Blue, violet, or purple colourations are also obtained in many instances by mixing phenols with strong sulphuric acid containing nitrous acid (Liebermann, B. 7, 248, 1098).

(2) Phenols behave as weak acids, dissolving in caustic alkalis with the formation of phenates, which are not decomposed by water.

(3) Like the tertiary alcohols of the fatty series, to which they bear considerable analogy, the phenols on treatment with fatty acids are found to have a small initial velocity and a low limit of etherification (Menschutkin, B. 11, 2151; A. 197, 220). Phenol ethers containing acid radicles are therefore prepared by treating the phenol with an acid chloride, thus

$$C_6H_5OH + CH_3.COCl = C_6H_5.O.COCH_3 + HCl.$$

A convenient means of conducting the reaction is to warm equimolecular proportions of the phenol and fatty acid with $\frac{1}{3}$ mol. prop. of phosphorus oxychloride (Nencki, J. pr. [2] 25, 282; Seifert, J. pr. [2] 31, 467).

(4) Phenol ethers containing alkyl radicles are obtained by digesting the potassium or sodium salts of the phenol either with an alkyl iodide (Cahours, A. 78, 226) or with a sulphovinate (Kolbe, J. pr. [2] 27, 424), thus:

$$C_6H_5OK + CH_3I = C_6H_5.O.CH_3 + KI.$$

The ethers are stable in the presence of alkalis, but on digestion with hydriodic or hydrochloric acids are decomposed into phenol and alkyl iodide or chloride, the method being employed for the preparation of pyrocatechol and other phenols from the ethers occurring in beechwood tar.

(5) On oxidation phenols exhibit no analogy with the tertiary fatty alcohols. Many phenols in alkaline solution are oxidised on exposure to the air with the formation of complex products of unknown composition. Those which contain hydroxyl- radicles in the para- or 1:4- position—*e.g.*, hydroquinone—yield quinones on oxidation with dilute chromic acid mixture or permanganate. In these cases the hydroxylic hydrogen is alone affected by the oxidising agent, and oxidation of the side chains in the homologues of phenol does not take place unless this is replaced by alkyl radicles, or preferably inorganic acid radicles (Heymann and Königs, B. 19, 705, 3304).

Fusion with caustic potash or caustic soda results in the production of polyhydric phenols in the case of the hydroxybenzenes, phenol, and resorcinol (*q. v.*). With phenols containing side chains, however, oxidation ensues with the production of hydroxy- acids, the rule being that when two or more alkyl- radicles are present the one adjacent to the hydroxyl first undergoes oxidation:[1] thus metaxylenol [Me:Me:OH = 1:3:4] yields successively orthohydroxymetatoluic acid [Me:COOH:OH = 1:3:4], and hydroxyisophthalic acid [COOH:COOH:OH = 1:3:4].

(6) Phenols can exchange hydroxyl for other radicles; thus the corresponding hydrocarbons result on distillation with zinc-dust (Baeyer, A. 140, 295), amidobenzenes are obtained in small quantity by heating with ammonia and zinc chloride at 280-300° (Merz and Weith, B. 13, 1298), and thiophenols with other thio- derivatives are produced by distillation with phosphorus pentasulphide (Kekulé, Z. 1867, 193; *cf.* Graebe, A. 179, 179).

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[1] Thymol is an exception, yielding in the first instance thymohydroxycumic acid [$COOH:OH:C_3H_7\beta = 1:3:4$].

(7) When heated with caustic soda or caustic potash, phenols combine with carbon dioxide forming hydroxy- acids (Kolbe, J. pr. [2] 10, 93; 11, 24; Ihle, J. pr. [2] 14, 454; Schmitt, J. pr. [2] 31, 407, Germ. Pat. 29939 of June 24, 1884; *cf.* Germ. Pat. 38742 of May 30, 1886; Kostanecki, B. 18, 3203). Hydroxy- acids also result when phenols are heated with carbon tetrachloride and caustic soda,

$$C_6H_5.ONa + CCl_4 + 5NaOH$$
$$= ONa.C_6H_4.COONa + 3H_2O + 4NaCl$$

(Reimer and Tiemann, B. 9, 1285; Hasse, B. 10, 2186; Schall, B. 12, 819), and hydroxy- aldehydes when chloroform is substituted for the tetrachloride (Reimer and Tiemann, B. 9, 824; Tiemann and Herzfeld, B. 10, 63; Tiemann and Schotten, B. 11, 772).

(8) Phenols yield substitution derivatives far more readily than the corresponding hydrocarbons; thus dilute nitric acid readily converts phenol into a mixture of ortho- and para- nitrophenol. The halogen and nitro- derivatives are more strongly acid in character than the phenols from which they are derived, the acid character being the more pronounced the greater the number of halogen atoms or nitro- groups introduced into the molecule—picric acid (trinitrophenol), for example, decomposing alkaline carbonates and forming salts of considerable stability.

The action of iodine in potassium iodide solution on phenates has been studied by Messinger and Vortmann (B. 22, 2312; *cf.* Farbenfab. vorm. F. Bayer & Co.'s Germ. Pat. 49739 of Mar. 9, 1889). Phenol yields a dark-red non-crystallisable triiodide $C_6H_3I_2.OI$, isomeric with the ordinary white triiodide. Cresols, thymol, carvacrol (Bayer & Co., Germ. Pat. 53752 of Feb. 23, 1890), isobutylphenol (*ibid.*, Germ. Pat. 56830 of Nov. 2, 1890), and resorcinol (*ibid.*, Germ. Pat. 52828 of Aug. 30, 1889) also give iodine derivatives, and the thymol compound $C_{20}H_{22}O_2I_3$ has been introduced as an iodoform substitute under the name annalidin (*cf.* Ph. J. [3] 20, 241).

For further information with regard to substitution derivatives of phenol other than trinitrophenol (*v.* Picric acid), nitrocresols (*v.* Victoria yellow), and nitrosophenols (*v.* Quinonoximes), Watts' Dictionary of Chemistry should be consulted.

I. Monohydric Phenols.

Phenol $C_6H_5.OH$.

Phenol or carbolic acid has already been described (*v.* Carbolic Acid). For medicinal purposes it is now prepared from aniline by the diazo- reaction (Ph. J. [3] 20, 241). So obtained it melts at 41–42°, boils at 181°, and has very little odour.

Phenols $C_7H_7.OH$.

The isomeric cresols have already been described (*v.* Cresol).

Phenols $C_8H_9.OH$.

Xylenols $C_6H_3Me_2.OH$.[1]

Occurrence.—A xylenol boiling at 219–220° occurs in beechwood-tar creosote in the fraction boiling at about 220° (Marasse, A. 152, 75; Tiemann and Mendelssohn, B. 10, 57). Xylenols, especially the 1:3:4- isomeride, are present in considerable quantities in the fraction of blast-furnace tar, boiling at 205–230° (Smith, Coutts and Brothers, C. J. 49, 22), and two xylenols, the 1:3:5- and 1:2:4- isomerides, are present in the coal tar fraction, boiling at 170–210° (Schulze, B. 20, 410).

Preparation.—The 1:2:4-, 1:3:2-, 1:3:4- and 1:4:2- xylenols have been obtained by fusing the corresponding xylenesulphonic acids with caustic potash; the remaining two isomerides have been prepared from the corresponding xylidines by the diazo- reaction.

Properties.—(1) 1:2:3- xylenol (Töhl, B. 18, 2562) crystallises in slender needles, melts at 75°, boils at 218°, and in aqueous solution gives a blue colour with ferric chloride.

(2) 1:2:4- xylenol (Jacobsen, B. 11, 28; 17, 161) forms long needles, melts at 62·5°, boils at 225° under 757 mm. pressure, and gives no colour with ferric chloride.

(3) 1:3:2- xylenol (Jacobsen, B. 11, 26; 21, 2828; Nölting and Pick, B. 21, 3154) forms scales or flat needles, melts at 49°, boils at 211–212°, and gives no colour with ferric chloride.

(4) 1:3:4- xylenol (Jacobsen, B. 11, 2052; Harmsen, B. 13, 1558) crystallises in needles, melts at 26° (Städel and Holz, B. 18, 2921), boils at 211·5° (Jacobsen, B. 18, 3464), and in aqueous solution is coloured blue, in alcoholic solution green, by ferric chloride.

(5) 1:3:5- xylenol (Töhl, B. 18, 362) crystallises in slender needles, melts at 68° (Nölting and Forel, B. 18, 2679), boils at 219·5°, and gives no colour with ferric chloride.

(6) 1:4:2- xylenol (Jacobsen, B. 11, 26) crystallises in large flat needles, melts at 74·5°, boils at 210° (Nölting, Witt, and Forel, B. 18, 2665), and gives no colour with ferric chloride.

Para-ethylphenol $C_6H_4Et.OH$ (Fittig and Kiesow, A. 156, 251; Errara, G. 14, 484; Auer, B. 17, 670).

Phenols $C_9H_{11}.OH$.

The following phenols are obtained either by fusing the corresponding potassium sulphonates with caustic potash or by the diazo- reaction from the corresponding cumidines:—

Hemellithol [Me_3:OH = 1:2:3:5] (Jacobsen, B. 19, 2518).

α-Pseudocumenol [Me_3:OH = 1:2:4:5] (Reuter, B. 11, 29; Liebermann and Kostanecki, B. 17, 885; Auwers, B. 17, 2976).

β-Pseudocumenol [Me_3:OH = 1:2:4:6] (Edler, B. 18, 629; Jacobsen, B. 19, 1218).

γ-Pseudocumenol [Me_3:OH = 1:2:4:3] (Engel, B. 18, 2229).

Mesitol [Me_3:OH = 1:3:5:6] (Biedermann and Ledoux, B. 8, 59, 250; Jacobsen, A. 195, 268).

Phenols $C_{10}H_{13}.OH$.

The three theoretically possible tetramethylphenols, durenol [Me_4:OH = 1:3:4:6:2] (Jacobsen and Schnapauff, B. 18, 2843), isodurenol [Me_4:OH = 1:3:4:5:2] (Jacobsen, B. 15, 1854), and prehnitol [Me_4:OH = 1:2:3:4:5] (Töhl, B. 21, 907), have been obtained from the corresponding tetramethylbenzenesulphonic acids by fusion with caustic potash.

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[1] The radicles are given in the order Me:Me:OH.

Carvacrol *Orthocymophenol, methylisopropylphenol* (*cf.* Widman, B. 24, 455) $C_6H_3Pr^{\beta}Me.OH$ [$Me:OH:Pr^{\beta} = 1:2:4$].

Occurrence.—It occurs in the ethereal oils of *Origanum hirtum* and *Satureja hortensis* (Jahns, J. 1879, 942; B. 15, 816), of *Satureja montana* (Haller, Bl. 37, 411), and also in small quantity in the oil of *Thymus serpyllum* (Jahns).

Formation.—It is obtained in good yield by carefully fusing a mixture of sodium cymenesulphonate with 3 parts of caustic potash (Pott, B. 2, 121; Müller, B. 2, 130; Jacobsen, B. 11, 1060), acidifying with hydrochloric acid and extracting with ether.

It is also formed from carvole, a constituent of cumin oil, by heating with glacial phosphoric acid, much heat being evolved in the reaction (Kekulé and Fleischer, B. 6, 934; Lustig, B. 19, 12).

Properties.—It is a thick oil, which solidifies at −20°, melts at about 0°, and boils at 236·5–237° (Stohmann, J. pr. [34] 319). Its alcoholic solution is coloured green by ferric chloride.

Thymol *Metacymophenol, methylisopropylphenol* (*cf.* Widman, B. 24, 455) $Pr^{\beta}(Me)C_6H_3.OH$ [$Me:OH:Pr^{\beta} = 1:3:4$].

Occurrence.—Thymol occurs in the essential oil of the common garden thyme, *Thymus vulgaris* (Doveri, A. 64, 374; Lallemand, A. Ch. [3] 49, 148), of the seeds of *Ptychotis Ajowan* (Stenhouse, A. 98, 307; Müller, B. 2, 130), of horsemint, *Monarda punctata* (Arppe, A. 58, 42), and together with some carvacrol in the oil of *Thymus serpyllum* (Jahns, B. 15, 819).

Preparation.—It is obtained from oil of thyme by shaking with aqueous soda, separating the undissolved terpene, and acidifying the alkaline extract with hydrochloric acid; the precipitated thymol is then crystallised from acetic acid.

Properties.—Thymol crystallises in large monoclinic (Miller, A. 93, 269) or hexagonal (Miller, A. 98, 310) prisms, melts at 51·5° (Stohmann, J. pr. [2] 34, 320), boils at 222° (Stenhouse, *l.c.*), at 230° (Lallemand, *l.c.*), and has an odour of thyme. It requires about 333 parts of water for its solution, but dissolves readily in alcohol and acetic acid. When heated with phosphorus pentoxide it yields *metacresol* and *propylene*, whilst with phosphorus pentasulphide it gives *cymene* (1:4-methylisopropylbenzene) (Fittica, A. 172, 305; *cf.* Widman, B. 24, 453).

Detection.—When an aqueous thymol solution is treated with $\frac{1}{2}$ part of acetic acid, and then with 1 part of sulphuric acid and warmed, it becomes red-violet. The reaction is a very delicate one, but only succeeds when the material is free from substances which are decomposed and coloured by sulphuric acid. This red solution gives a broad absorption band at E and a less strongly marked one at D (Wolff, Fr. 22, 96). For other tests *v.* Hirschsohn (Fr. 22, 574) and Bornträger (Fr. 29, 572).

Paraisobutylphenol is obtained by heating phenol (10 parts), isobutyl alcohol (8 parts), and zinc chloride (24 parts) at 180° (Liebmann, B. 14, 1842; 15, 150; Actieng. für Anilinfab., Germ. Pat. 17311 of July 10, 1881, expired Nov. 1883). It crystallises in needles, melts at 97·5–98°, boils at 236–238° (*cf.* Studer, A. 211, 242), and has an odour resembling that of thymol.

II. DIHYDRIC PHENOLS.

Phenols $C_6H_4(OH)_2$.

The three theoretically possible isomerides of this formula are known.

Pyrocatechol *Pyrocatechin, catechol*

$$C_6H_4(OH)_2\ [OH:OH = 1:2].$$

Occurrence.—Pyrocatechol has been detected in the autumnal leaves of the Virginia creeper (*Ampelopsis hederacea*) (Gorup Besanez, B. 4, 905), in the various kinds of kino (Flückiger, B. 5, 1), and in crude beet-root sugar (Lippmann, B. 20, 3298).

Formation.—Pyrocatechol is obtained by the dry distillation of morintannic acid contained in fustic (Wagner, J. pr. 51, 95; 52, 450; 55, 65), of various catechins: hence the name pyrocatechin (Zwenger, A. 37, 327; Wackenröder, A. 37, 309), of all tannins which turn ferric salts green (Eissfeldt, A. 92, 109, compare Uloth, A. 111, 219), of protocatechuic acid (Strecker, A. 118, 285; Tiemann and Haarmann, B. 7, 618), and of wood. It occurs, therefore, in crude pyroligneous acid, the proportion amounting to 0·1–0·2 p.c. according to Buchner (A. 96, 188). It is also formed in small quantity by heating filter-paper at 200°, or starch or sugar at 280°, with water for from 4 to 6 hours (Hoppe-Seyler, B. 4, 15).

It is obtained pure and free from its isomerides when orthiodophenol (Lautemann, A. 120, 315; Körner, Z. 1868, 322; Nölting and Stricker, B. 20, 3019) and orthophenolsulphonic acid (Kekulé, Z. 1867, 643; Barth and Senhofer, B. 9, 972; Degener, J. pr. [2] 20, 300) are fused with caustic potash. It is also formed, together with resorcinol as chief product, when orthochlorophenol (Nölting, B. 9, 1794) and orthobromophenol (Fittig and Mager, B. 8, 363) are fused with caustic potash, whilst metabromophenol likewise gives a mixture of pyrocatechol and resorcinol under similar conditions (Fittig and Mager, *ibid.* 365).

Preparation.—(1) Pyrocatechol can be prepared from its methyl-salt, guaiacol, which forms the chief constituent of the fraction of Rhenish beechwood-tar creosote boiling at 200–205°, by heating it at 195–200° in a retort attached to a condenser and passing a current of gaseous hydrogen iodide through it until methyl iodide no longer distils over and red streaks make their appearance on the sides of the flask. The operation is then stopped to avoid the formation of decomposition products, the contents of the retort fractionated, and the fraction boiling at 220–250° is further purified by crystallisation from benzene. The yield of pyrocatechol from 1 kilo. of beechwood-tar creosote boiling at 200–205° amounts to about 46 grams (Baeyer, B. 8, 155). According to Perkin, jun. (C. J. 57, 587), an almost quantitative yield can be obtained by slightly modifying the method, and employing fuming aqueous hydrogen iodide (sp.gr. = 1·96) instead of the gas. A solution of guaiacol in $1\frac{1}{2}$ times its weight of fuming hydriodic acid is gently heated for about an hour in an apparatus attached to a condenser (to condense the eliminated methyl iodide), allowed to cool slightly, mixed with $\frac{1}{4}$ its weight of hydriodic acid, and heated as before for an hour. The product, after washing with water, is extracted with ether, the ether removed by distillation, and the residual oil purified by rapid fractionation.

(2) Pyrocatechol can be obtained perfectly pure by fusing phenolorthosulphonic acid with 24 mol. props. of caustic potash at 320–330°, the yield then amounting to about 20 p.c. of the theoretical. By using less potash or a lower temperature a smaller yield is obtained, as is also the case when the fusion is effected at 400° (Degener, J. pr. [2] 20, 307).

Properties.—It crystallises from water in prismatic needles and from benzene in broad scales, melts at 104° (Fittig and Mager, *l.c.*), boils at 240–245° (Wagner), at 245° under a pressure of 730 mm. (Graebe, A. 254, 296), and is readily soluble in water, alcohol, ether, and benzene. Its aqueous solution reduces solutions of the salts of the noble metals, and precipitates cuprous oxide from Fehling's solution on gently warming, and its alkaline solution rapidly becomes brown on exposure to the air.

Reactions.—When heated with phthalic anhydride and an excess of sulphuric acid at 140° it is converted into *alizarin* (Baeyer and Caro, B. 7, 972) and *hystazarin* (Liebermann, B. 21, 2501; Schöller, B. 21, 2503), and when heated with phthalic anhydride and zinc chloride at 140° yields *pyrocatecholphthaleïn* (Baeyer and Kochendörfer, B. 22, 2196).

Pyrocatechol also forms condensation compounds with amines; thus, when heated with orthophenylenediamine it yields *phenazine* (Ris, B. 19, 2206), and with orthamidophenol and orthamidothiophenol yields *phenoxazine* (Bernthsen, B. 20, 942) and *thiodiphenylamine* (Bernthsen, B. 19, 3255) respectively.

Detection.—Pyrocatechol in aqueous solution, on treatment with aqueous ferric chloride gives an emerald-green colour, which changes to a violet-red on addition of sodium carbonate (Hlasiwetz and Barth, A. 130, 353). The reaction succeeds best if a 4 p.c. ferric chloride solution is employed and sodium bicarbonate is substituted for the carbonate (Ebstein and Müller, Fr. 15, 465).

Estimation.—The aqueous solution of pyrocatechol is precipitated with a concentrated solution of lead acetate and the precipitate rapidly washed with water 5 or 6 times to free it from the excess of lead acetate, dried at 100–110°, and weighed. The precipitate has the composition $C_6H_4O_2Pb$, and is very sparingly soluble in water but readily soluble in acetic acid (Degener, J. pr. [2] 20, 320; compare Zwenger, *l.c.*).

Derivatives.—Guaiacol $OH.C_6H_4.OMe$ is formed in the dry distillation of guaiacum resin (Sobrero, A. 48, 19; Völckel, A. 89, 349); by heating the calcium salt of vanillic acid with lime (Tiemann, B. 8, 1123); by heating molecular proportions of pyrocatechol, caustic potash, and potassium methyl sulphate at 170–180° (Gorup Besanez, A. 147, 248); and occurs in beechwood-tar creosote (Hlasiwetz, A. 106, 362). To obtain it from the last-named source, the fraction boiling at 200–205° is repeatedly shaken with tolerably strong ammonia, then washed with water and rectified. The product is then dissolved in an equal volume of ether, and the potassium salt which separates on addition of a slight excess of concentrated alcoholic potash is washed with ether, recrystallised from alcohol, and finally decomposed by dilute sulphuric acid.

The barium salts of guaiacol and creosol are much less soluble in water than those of the admixed phenols, and afford a means of rapidly and cheaply purifying these substances; 40 kilos. of beechwood-tar creosote are mixed with a solution of 64 kilos. of crude barium hydrate in 150 litres of hot water. On cooling, the crystalline magma is filtered off, pressed, washed once with water, and the guaiacol, which is mixed with more or less creosol, separated by the addition of hydrochloric acid and subsequent steam distillation. The distillate on treatment with aqueous caustic potash gives the sparingly soluble crystalline salts of guaiacol and creosol, the two phenol ethers being finally separated by rectification (Dr. v. Heyden's Nachfolger, Germ. Pat. 56003 of Aug. 5, 1890).

Properties.—Guaiacol is an oil, which boils at 200°, has a sp.gr. = 1·117 at 13° (Hlasiwetz), an aromatic odour, and in alcoholic solution gives an emerald-green colour with ferric chloride. Digestion with hydriodic acid (Baeyer, B. 8, 155) or hydrochloric acid (Perkin, jun., C. J. 57, 589) converts it into *pyrocatechol.* When heated with phthalic anhydride and stannic chloride it yields *guaiacolphthaleïn* (Baeyer and Kochendörfer, B. 22, 2199).

Veratrol $C_6H_4(OMe)_2$ is obtained by distilling veratric acid with baryta (Merck, A. 108, 60) and by the methylation of the potassium salt of guaiacol (Marasse, A. 152, 74). It is an oil which solidifies at 15°, boils at 205–206°, and has a sp.gr. = 1·086 at 15°.

Resorcinol *Resorcin* $C_6H_4(OH)_2[OH:OH = 1:3]$.

Formation.—Resorcinol was first obtained by fusing galbanum and gum-ammoniac (Hlasiwetz and Barth, A. 130, 354), asafœtida (*ibid.* A. 138, 63), acaroid-resin and *sagapenum* (*ibid.* A. 139, 80), and probably all resins which yield umbelliferone on dry distillation (*ibid.* A. 139, 83; compare Hlasiwetz and Grabowski, A. 139, 100) with caustic potash, and received its name resorcinol on account of its production from resins and similarity to orcinol. It is also formed by the dry distillation of brasilin (Kopp, B. 6, 447).

It is obtained by fusing metiodophenol (Körner, Z. 1868, 322; Nölting and Stricker, B. 20, 3021), phenolmetasulphonic acid (Barth and Senhofer, B. 9, 972), or benzenemetadisulphonic acid (Garrick, Z. 1869, 551; Barth and Senhofer, A. 174, 238; Degener, J. pr. [2] 20, 318) with caustic potash, and its connection with the metaseries is established by its formation by the diazo- reaction from metamidophenol (Bantlin, B. 11, 2101).

It is, moreover, formed as sole product when chlorobenzeneparasulphonic acid (Oppenheim and Vogt, A. Supplb. 6, 376), benzeneparadisulphonic acid, owing to the intermediate formation of phenolmetasulphonic acid (Barth and Senhofer, B. 8, 1483), and parabromophenol (Fittig and Mager, B. 7, 1177) are fused with caustic potash; whilst orthochlorophenol (Nölting, B. 9, 1794) and orthobromophenol (Fittig and Mager, B. 8, 364) give pyrocatechol, and parachlorophenol (Petersen, B. 6, 1399) and pariodophenol (Körner, Z. 1868, 322; Nölting and

Wrzesinski, B. 8, 820) give hydroquinone in addition under like conditions. Nölting and Stricker (B. 20, 3022) point out that this seeming intramolecular change is probably due to the alkali acting, in the first instance, as an oxidising, and subsequently as a reducing agent; the formation of resorcinol from parabromophenol being represented by the equations:

$$(1)\ C_6H_4Br.OH + O$$
$$= OH.C_6H_3Br.OH[OH{:}OH{:}Br = 1{:}3{:}4].$$
$$(2)\ OH.C_6H_3Br.OH + H_2 = OH.C_6H_4.OH + HBr.$$

Preparation.—Resorcinol is usually prepared by fusing benzenemetadisulphonic acid with caustic alkali.

1. Mühlhaüser has given in considerable detail an account of the manufacture of resorcinol as carried on at the present day (D. P. J. 263 (1887), 154), and Schoop has also described the process in almost the same words, adding to his paper illustrations drawn to scale of the plant employed (Zeit. für Chem. Ind. 1887, part 13, p. 1). Benzenemonosulphonic acid is first prepared by treating 60 kilos. of pure benzene (free from thiophen) with 300 kilos. of sulphuric acid of 67°Bé. in a cast-iron pan provided with an agitator and a leaden reflux condenser. To bring about the reaction the mixture is continually stirred for about 10 hours, and a very gentle heat applied by means of steam. For the purpose of preparing the disulphonic acid, the monosulphonic acid dissolved in the excess of sulphuric acid is run into a second cast-iron pan (fitted with an agitator and a condenser), mixed with 85 kilos. of powdered and perfectly dry (? sodium) sulphate, and heated in an oil bath so that the temperature of the mixture remains at 225° for eight hours. During the first half of this time benzene to the amount of about 10 kilos. distils over, and is collected, whilst sulphurous acid is evolved and escapes. The product is stirred into 1500 litres of water, and converted into sodium salt in the usual way, which, after thoroughly drying, is powdered and sieved. The yield amounts to about 200 kilos. For the fusion with alkali, 250 kilos. of caustic soda and 10 kilos. of water are heated over a direct flame in a cast-iron pot (provided with stirring apparatus) until the molten mass is judged to be sufficiently hot to remain liquid on addition of the sodium salt; this temperature being reached when a little common salt thrown in dissolves rapidly with a hissing sound. The stirrer is then set in motion, 125 kilos. of the dry sulphonate are quickly introduced, and when the melt has become brown and gives no further evidence of reaction it is ladled out, cooled, broken up, and dissolved in 500 litres of water. Hydrochloric acid is then added to acid reaction, the liquor extracted by four successive treatments with purified amyl alcohol in quantities of 100 kilos., the latter removed by distillation with steam, and the residual liquor in the still evaporated to dryness in an enamelled pan. To purify the resorcinol thus obtained it is distilled in a vacuum apparatus; water and phenol pass over first, and when the temperature reaches 190° the pressure is decreased to 30 mm., with the result that resorcinol begins to distil over. The yield of pure product amounts to about 19–23 kilos. from the 125 kilos. of benzenedisulphonate employed, or to about 50 p.c. of the theoretical, calculated on the benzene actually employed.

2. To prepare the benzenemetadisulphonic acid, 90 kilos. of fuming sulphuric acid are placed in a cast-iron vessel provided with a stirring apparatus, and attached to a reflux condenser, and 24 kilos. of chemically-pure benzene are gradually run in with continual stirring; the temperature gradually rises to the boiling-point of benzene, and in the course of two to three hours the benzene is completely converted into monosulphonic acid. The reflux condenser is then removed, the vessel attached to a condenser arranged in the ordinary way, and the temperature raised to 275° in order to convert the mono- into di- sulphonic acid. Any benzene which comes over with the water given off at this stage of the reaction is collected in the receiver. After about twenty minutes heating at this temperature the melt is allowed to cool, then poured into 2000 litres of water, neutralised with milk of lime, and converted into sodium salt in the usual way, the solution of the sodium salt being eventually evaporated to dryness. To obtain resorcinol from this product, 60 kilos. of the completely dry sodium salt are added to 150 kilos. of caustic soda dissolved in the smallest possible quantity of water, and the mass heated at 270° in a cast-iron vessel with continual stirring for eight to nine hours, during which time it becomes gradually semi-solid and finally solid. On cooling, the melt is dissolved in 500 litres of boiling water, and the solution acidified with hydrochloric or sulphuric acid, and boiled until all sulphur dioxide has escaped. The tarry matter which is deposited is then filtered off from the cold solution, and the filtrate systematically extracted with ether in a copper extraction apparatus, the ether being subsequently distilled off and recovered. The crude resorcinol so obtained is a colourless, crystalline mass, which can be freed from traces of ether and water by heating it at 215° in an enamelled vessel. It then forms a hard, brittle mass, containing 92–94 p.c. of resorcinol, together with some phenol, and about 5 p.c. of tarry matter; and to free it from these impurities it is distilled, water coming over first, then phenol, and finally resorcinol, which can be further purified by sublimation or by crystallisation from benzene. An almost theoretical yield of resorcinol is said to be obtained by this method (Bindschedler and Busch, Monit. Sci. 1878, 1169; W. J. 1878, 1080).

Properties.—Resorcinol crystallises from benzene in needles, and from water, alcohol, or ether in tables or short, thick, rhombic prisms (Groth, B. 3, 450), melts at 119° (Calderon, C. R. 84, 780), boils at 276·5° under a pressure of 759·5 mm. (*ibid.*), at 280° under a pressure of 730 mm. (Graebe, A. 254, 296), sublimes at lower temperatures in lustrous, silky needles, and is volatile with steam. It is readily soluble in water, of which 100 parts dissolve 86·4 parts of resorcinol at 0°, 147·3 parts at 12·5°, and 228·6 parts at 30° (Calderon), and is still more soluble in alcohol and ether, but dissolves sparingly in chloroform, carbon bisulphide, and cold benzene. Its taste is intensely sweet, but afterwards causes irritation. On exposure to the air it becomes red, and an ammoniacal solution exposed to the air becomes rose-red, then brown, and deposits flocks of an orceïn-like substance (Malin, A. 138, 76). It readily reduces Fehling's solution and ammoniacal silver solution on warming.

Reactions.—Bromine readily converts resorcinol into tribromoresorcinol (Hlasiwetz and Barth, A. 130, 357; Fittig and Mager, B. 7, 1178; Weselsky and Benedikt, M. 4, 227); nitric acid converts it into *trinitroresorcin* (styphnic acid); nitrous acid reacts with it forming, according to the conditions employed, either *nitroso-derivatives* (*v.* SOLID GREEN) or *resazurin* and *resorufin* (Nietzki, Dietze, and Mäckler, B. 22, 3020); and concentrated sulphuric acid converts it into sulphonic acids, of which the disulphonic acid is the best known (Piccard and Humbert, B. 9, 1480; Tedeschi, B. 12, 1267; Merz and Zetter, B. 12, 2037; Fischer, M. 2, 231).

On fusion with a considerable excess of caustic soda, resorcinol yields a product containing 60–70 p.c. of *phloroglucinol*, 2–3 p.c. of *pyrocatechol*, and 1·5 p.c. of *diresorcinol* (Barth and Schreder, B. 12, 503)

When heated with phthalic anhydride, resorcinol is converted into *fluoresceïn* (Baeyer, B. 4, 558, 662; 7, 1211); when heated with phthalic anhydride, benzyl chloride, and sulphuric acid it yields *chrysolin* (Reverdin, Monit. Sci. 7, 860; W. J. 1877, 915; *v.* TRIPHENYLMETHANE COLOURING MATTERS); and when heated with benzotrichloride it forms resorcinolbenzeïn (*v.* AURINE AND ROSOLIC ACID).

Resorcinol also yields a series of condensation compounds which dissolve in alkalis, forming coloured solutions. Thus, when heated with anhydrous oxalic acid under pressure at 200°, it is converted into *resorcinoxalcïn* $C_{20}H_{14}O_7$, which dissolves in alkalis forming red solutions, showing, when dilute, an intense moss-green fluorescence (Claus, B. 10, 1305; 14, 2563); when heated with oxalic acid and dehydrating agents, such as sulphuric or phosphoric acids, it yields two dyes having the composition $C_{14}H_8O_5$, of which one dissolves in alkalis, forming reddish-yellow solutions showing a green fluorescence, and the second forms brown non-fluorescent solutions (Gukassianz, B. 11, 1184); and, when heated with tartaric acid and 1 p.c. of sulphuric acid, it forms *resorcintartreïn*, a dark olive-green powder, which dissolves in alkalis with a dark-red colour, yielding strongly fluorescent solutions (Fraude, B. 14, 2558).

Detection.—Small quantities of resorcinol can be detected by heating with phthalic anhydride for a few minutes, dissolving the melt in dilute alkali, preferably ammonia, and pouring into water, the presence of resorcinol being shown by the production of a green fluorescent solution owing to the formation of fluoresceïn. In aqueous solution, resorcinol gives a dark-violet colour with ferric chloride, and is not precipitated by lead acetate, thus differing from pyrocatechol, whilst, when warmed with manganese dioxide or other oxidising agents, it gives no odour of quinone, thus differing from hydroquinone.

When resorcinol is warmed at 100° for a short time with sulphuric acid, to which some finely powdered sodium nitrite has been added, and the melt is poured into water, rendered alkaline with ammonia, and shaken with fusel oil, the oily layer is coloured a carmine-red and shows a cinnabar-red fluorescence (Bindschedler, M. 5, 169).

Estimation.—Resorcinol can be estimated quantitatively by titration with bromine water or a solution of bromine in alkali, as in the case of phenol (*v.* CARBOLIC ACID), the method being based on the fact that bromine water reacts with it, forming tribromoresorcinol, according to the equation

$$C_6H_4(OH)_2 + 3Br_2 = C_6HBr_3(OH)_2 + 3HBr$$

(Degener, J. pr. [2] 20, 322).

A second method, also due to Degener (*l.c.*), consists in adding a sufficient quantity of potassium iodide and alkali to the very dilute aqueous solution of resorcinol, and treating with a slight excess of an aqueous solution of bleaching-powder. Dilute hydrochloric acid is then added in just sufficient quantity to dissolve the precipitated lime, sodium hyposulphite (thiosulphate) solution rapidly run in until all colour has disappeared, and the excess titrated back with iodine. It is necessary that the standard solutions of bleaching-powder, sodium hyposulphite, and iodine should be very dilute. Triiodoresorcinol is formed in the reaction as a flocculent precipitate varying in colour from rose-red to white.

Impurities.—Commercial resorcinol is usually met with in a fairly pure state, the chief impurities being phenol and water. Occasionally it contains small quantities of thioresorcinol, which are formed in the potash fusion by the action of nascent hydrogen on the benzenedisulphonate. This impurity can be removed by treating the aqueous solution with lead acetate, with which it forms an insoluble yellow compound (Pazschke, J. pr. [2] 2, 418; Nölting, Post's Zeit. für Chem. Grossgew. 1879, 131).

Hydroquinone *Quinol* $C_6H_4(OH)_2[OH:OH = 1:4]$.

Formation.—Hydroquinone is formed by the dry distillation of quinic acid (Wöhler, A. 51, 146) and hydroxysalicylic acid (Rakowski and Leppert, B. 8, 789), and, together with resorcinol, by fusing pariodophenol (Nölting and Wrzesinski, B. 8, 820) or euxanthone, a product obtained from Indian yellow (*q. v.*) (Graebe, A. 254, 296) with caustic potash. It is also obtained when quinone is reduced with sulphurous acid (Wöhler, A. 51, 151); when the glucoside arbutin is hydrolysed by boiling with dilute sulphuric acid (Strecker, A. 107, 229); when para-diazophenol sulphate is boiled with 10–15 p.c. aqueous sulphuric acid (Weselsky and Schuler, B. 9, 1160); and when a solution of nitrosophenol in aqueous soda is gently treated with hydroxylamine hydrochloride (Hepp, B. 10, 1654). It has been prepared synthetically by Hermann from ethyl succinosuccinate (A. 211, 336).

Preparation.—Hydroquinone is best obtained by the oxidation of aniline. For this purpose a concentrated aqueous solution of sodium bichromate is gradually added to a well-cooled (5°–10°) solution of 1 part of aniline in 8 parts of sulphuric acid and 25 parts of water. The mixture at first becomes dark green, and towards the end of the operation a deep blue-black; a further addition of the bichromate solution brings about the solution of the greater part of the precipitate, and a brown, turbid liquid is obtained containing quinone and quinhydrone in suspension. The quinone and quinhydrone are then reduced to hydroquinone by passing sulphur dioxide through the liquid until it contains free sulphurous acid, the suspended matter filtered off, and the hydroquinone extracted from the filtrate by means of ether, which is subsequently distilled off. The yield of crude hydroquinone under these conditions amounts to as much as 85 p.c.; but with potassium bichromate, which must be used in a state of powder on account of its sparing solubility in water (B. 10, 1935, 2005; 11, 1103), the yield is much smaller (Nietzki, B. 19, 1468). In order to purify the product it is dissolved in the smallest possible quantity of hot water, and the solution boiled with animal charcoal and a little sulphurous acid, and allowed to crystallise (Ekstrand, B. 11, 713).

Properties.—Hydroquinone is dimorphous (Lehmann, J. 1877, 566). It crystallises from water in long hexagonal prisms (Groth, B. 3, 450), which, on heating, sublime in monoclinic scales. It has a slightly sweet taste, melts at 169° (Hlasiwetz and Habermann, B. 8, 684), boils at 285° under a pressure of 730 mm. (Graebe, A. 254, 296), dissolves in 17 parts of water at 15° and 10·5 parts at 28·5°, is readily soluble in alcohol, ether, and hot water, and very sparingly soluble in cold benzene. Its alkaline solution becomes brown on exposure to the air. It reduces Fehling's solution in the cold and ammoniacal silver nitrate on warming owing to the formation of quinone, and this oxidation to quinone is also effected by ferric chloride, nitric acid, chlorine, a mixture of potassium bichromate and sulphuric acid, &c. When its vapour is passed through a tube heated to low redness it is decomposed into hydrogen and quinone (Hesse, A. 114, 297).

Reactions.—It remains unchanged when fused with caustic potash (Wölz, A. 168, 91); but on fusion with 10 times its weight of caustic soda until hydrogen ceases to be evolved it yields *hydroxyquinol*, together with *diquinol* and *δ-hexahydroxydiphenyl* (Barth and Schreder, M. 5, 590).

When heated with phthalic anhydride and sulphuric acid it yields *quinizarin* (Grimm, B. 6, 508), and when heated with phthalic anhydride and zinc chloride it yields the colourless *hydroquinonephthaleïn* (Grimm, B. 6, 506; Ekstrand, B. 11, 714).

Phenols $C_7H_6(OH)_2$.

Cresorcinol *Cresorcin* (cresol-resorcin), *α-isorcin* (Hakansson), *lutorcin* (Vogt and Henninger), $C_6H_3Me(OH)_2[Me:(OH)_2=1:2:4]$.

Preparation.—Cresorcinol is best prepared by the diazo- reaction from orthamidoparacresol (Knecht, B. 15, 301, 1069; Nevile and Winther, B. 15, 2981) or paramido-orthocresol (Wallach, B. 15, 2835; Nölting, B. 19, 137). It may also be obtained by fusing bromoparacresol with caustic potash (Vogt and Henninger, C. R. 94, 650), and, together with salicylic acid, by fusing *α*-toluenedisulphonic acid (Hakansson, B. 5, 1084; Nölting, *l.c.*) and *γ*-toluenedisulphonic acid (Senhofer, A. 164, 131; *cf.* Claesson and Berg, B. 13, 1170) with caustic potash.

Properties.—It crystallises in spherical aggregates or needles, melts at 104°–105°, boils at 267°–270°, and is readily soluble in water, alcohol and ether, sparingly soluble in benzene. It closely resembles resorcinol in many of its reactions—*e.g* with ammoniacal silver solution, bromine, phthalic anhydride, &c.—but differs from it by not forming colours when heated with nitrobenzene and sulphuric acid (Knecht, *l.c.*). Ferric chloride colours its aqueous solution a greenish-blue.

Toluquinol *Toluhydroquinone*

$$C_6H_3Me(OH)_2[Me:(OH)_2=1:2:5].$$

Preparation.—Toluquinol can be prepared from orthotoluidine by oxidation with chromic acid mixture (Nietzki, B. 10, 834, 1935), or from metamido-orthocresol by the diazo- reaction (Nevile and Winther, B. 15, 2979).

Properties.—It crystallises in scales, melts at 124°, is readily soluble in water, alcohol and ether, less soluble in benzene, yields toluquinone on oxidation (the aqueous solution being coloured brown-red by ferric chloride), and when heated with phthalic anhydride and excess of sulphuric acid is converted into *methylquinizarin* (Nietzki, B. 10, 2011).

Dihydroxytoluene $[Me:(OH)_2=1:2:6]$ crystallises in needles melting at 63–66° (Ullmann, B. 17, 1963).

Homocatechol *Homopyrocatechol*

$$C_6H_3Me(OH)_2[Me:(OH)_2=1:3:4].$$

Preparation.—Homocatechol is obtained by heating cresol with hydriodic acid (Müller, C. N. 10, 269) and from metamidoparacresol by the diazo- reaction (Nevile and Winther, B. 15, 2983).

Properties.—It is a syrup which dissolves readily in the ordinary solvents, reduces Fehling's solution and ammoniacal silver solution in the cold, and in aqueous solution gives a green colouration with ferric chloride.

Derivative. — Creosol (creosote-guaiacol), *homoguaiacol* $[Me:OMe:OH=1:3:4]$, occurs in beechwood-tar creosote, and in the products obtained on submitting guaiacum resin to dry distillation (Hlasiwetz, A. 106, 339), and can be isolated from the creosote fraction boiling at 217–222° by dissolving it in an equal volume of ether, treating with $1\frac{1}{2}$–2 vols. of a saturated solution of alcoholic potash and decomposing the potassium salt which separates in the cold with dilute sulphuric acid. The mother-liquors contain some creosol potassium salt together with the potassium compound of phlorol (Hlasiwetz, *l.c.*; Tiemann and Mendelssohn, B. 10, 57; *v.* Guaiacol, *supra*).

It is a colourless oil which boils at 219–220°, has a faint but pleasant aromatic odour, and in alcoholic solution gives an emerald-green colour with ferric chloride (Tiemann and Nagai, B. 10, 207).

Orcinol *Orcin* $C_6H_3Me(OH)_2[Me:(OH)_2=1:3:5]$ (Tiemann and Streng, B. 14, 1999).

Occurrence and Formation.—Orcinol occurs in the free state in the various lichens (species *Variolaria*, *Roccella*, and *Lecanora*) which are employed in the preparation of archil and litmus, and can be prepared by boiling them with milk of lime. It follows, therefore, that it may also be prepared by a like method from the various acids, *e.g.* orsellic acid, lecanoric acid, evernic acid, &c., and ether-like compounds such as erythrin, picroerythrin, &c., which can be isolated from these lichens; orsellic acid, moreover, yields it also by dry distillation (Dumas, A. 27, 140; Schunck, A. 41, 159; 54, 269; Stenhouse, A. 68, 57, 99; Tr. 1848, 63; C. J. 20, 221; Strecker, A. 68, 108; De Luynes, A. Ch. [4] 6, 184; Lamparter, A. 134, 256).

It is also formed in small quantity together with parahydroxybenzoic acid by fusing aloes with caustic soda (Hlasiwetz, A. 134, 288).

It can also be prepared by fusing toluenemetadisulphonic acid or certain halogen derivatives of toluene, toluenemetasulphonic acid, or metacresol with caustic potash (Winther, Germ. Pat. 20713, of October 25, 1881, exp. February 1884; Nevile, Eng. Pat. 4389, of 1881) and by the diazo- reaction from metamidometacresol (Nevile and Winther, B. 15, 2987).

Preparation.—1. From lichens, preferably *Roccella tinctoria* or *fuciformis*. The lichen is macerated with milk of lime, and the strained liquor boiled for some hours and concentrated in order to decompose the acids and ether-like compounds in the extract. Carbon dioxide is then passed through so long as a precipitate falls, or the concentrated liquor is exactly neutralised with dilute sulphuric acid, and the filtrate evaporated nearly to dryness on a water-bath. The orcinol is extracted from the residue by means of benzene (in which erythrol, which is also produced in the decomposition of erythrin, is insoluble), and when the benzene solution is shaken up with about one-tenth its bulk of water, the orcinol is taken up by the latter and can be obtained on evaporation (Stenhouse, C. J. 20, 222). The crude product can be purified by distillation in a vacuum (De Luynes, *l.c.*).—2. Parachlorotoluene on sulphonation yields two sulphonic acids, which can be separated by fractional crystallisation of their barium salts. The acid yielding the less soluble barium salt gives on fusion with twice its weight of caustic potash at 280-300° a mixture of orcinol, salicylic acid, and a small proportion of parahydroxybenzoic acid and paracresol (Vogt and Henninger, Bl. 21, 373).

Properties.—Orcinol crystallises with one mol. prop. H_2O in 6-sided monoclinic prisms, melts when anhydrous at 86° (Lamparter, *l.c.*; Stohmann, J. pr. [2] 34, 315); at 106·5–108° (Nevile and Winther, B. 15, 2988); boils at 287–290° with slight decomposition (Dumas, *l.c.*), and dissolves readily in water, alcohol, and ether, less readily in benzene, and sparingly in chloroform. Its taste is sweet, but unpleasant. It rapidly becomes reddened on exposure to moist air, and its aqueous solution is coloured a deep violet by ferric chloride, and a dark red, soon changing to yellow, by bleaching-powder. Exposed to air in the presence of ammonia it is converted into *orceïn*, the chief constituent of archil, and becomes coloured a deep red-violet (Robiquet, A. 15, 292; Liebermann, B. 7, 247; 8, 1649; Zulkowski and Peters, M. 11, 227); and when heated with ammonia and hydrogen peroxide, it gives a red-violet colour (Wurster, B. 20, 2939).

Reactions.—On fusion with caustic soda, it yields much *resorcinol*, together with some *phloroglucinol*, *pyrocatechol*, and *tetrahydroxydiphenylmethane*; whilst if the fusion is long continued *phloroglucinol* is almost the sole product (Barth and Schreder, M. 3, 645).

When warmed in alkaline solution with chloroform it becomes at first purple and then fiery-red, and the product on dilution with water shows an intense greenish-yellow fluorescence, owing to the formation of *homofluoresceïn* (Schwarz, B. 13, 543). When heated with phthalic anhydride and sulphuric acid *orcinolphthaleïn* is obtained (E. Fischer, B. 7, 1214), which, unlike fluoresceïn, is colourless.

Detection and Estimation.—Orcinol may be detected by the homofluoresceïn test (*v. supra*), and can be estimated quantitatively, according to Reymann (B. 8, 790), by adding bromine-water of known strength in excess to a very dilute aqueous solution, and estimating the excess by addition of potassium iodide and titration with sodium thiosulphate. The bromine water should be titrated with pure orcinol. In this reaction tribromorcinol is precipitated.

Phenols $C_8H_8(OH)_2$.

Betorcinol *Homorcinol*, *paraxylorcinol* $C_6H_2Me_2(OH)_2$ [Me:Me:OH:OH = 1:4:3:5, *cf.* Kostanecki, B. 19, 2321].

Preparation.—Betorcinol is obtained from the lichen *Usnea barbata*, and from barbatic acid which occurs in it, by treatment with lime (Stenhouse and Groves, C. J. 37, 366). It has also been obtained, together with orcinol, from *Roccella fuciformis* (Lamparter, A. 134, 248).

Properties.—It forms quadratic crystals, melts at 163°, boils at 277–280°, and is less soluble in water than orcinol. Ferric chloride colours its aqueous solution a light carmine red. Its ammoniacal solution, like that of orcinol, is very rapidly coloured red on exposure to air. When heated with chloroform and caustic soda it gives a deep-red colour, and the solution in water shows a green fluorescence. Unlike orcinol, it does not yield a fluoresceïn when heated with phthalic anhydride; like orcinol, however, it forms a colourless phthaleïn, *betorcinolphthaleïn*, when heated with phthalic anhydride and sulphuric acid (Knecht, B. 15, 1070).

Metaxylorcinol $C_6H_2Me_2(OH)_2$ [Me:Me:OH:OH = 1:3:4:6, *cf.* Pfaff, B. 16, 1138; Kostanecki, B. 19, 2324] does not give a red colour on exposure in ammoniacal solution to the air.

Phenols $C_9H_{10}(OH)_2$.

Mesorcinol [Me_3:$(OH)_2$ = 1:3:5:2:6] is prepared by the diazo-reaction from amidomesitol (Knecht, B. 15, 1375). It forms white lustrous scales, which melt at 149° and boil at 274–275°. With ferric chloride it gives first a green colouration and then a grey precipitate, and when heated with sulphuric acid it yields a compound which dissolves in alkalis forming a rose-coloured solution showing, when dilute, an intense green fluorescence.

A phenol of this composition occurs in the form of its monomethyl ether as **cœrulignone oil** (cœrulignol) $OH.C_9H_{10}.OMe$ in the fraction of beechwood tar creosote boiling at about 240°; the methyl salt is characterised by giving in alcoholic solution a blue colour with baryta-water, and a green with ferric chloride, and in an aqueous solution a carmine-red precipitate with ferric chloride (Pastrovich, M. 4, 189).

III. Trihydric Phenols.

Phenols $C_6H_3(OH)_3$.

Pyrogallol *Pyrogallic acid* $C_6H_3(OH)_3$ $[(OH)_3 = 1:2:3]$.

Formation.—Pyrogallol is obtained by the dry distillation of gallic acid (Braconnot, A. Ch. [1] 46, 207; Pelouze, A. 10, 159); hence its name. It is also formed by fusing α- or β-parachlorophenolsulphonic acid (Petersen and Baehr-Predari, A. 157, 136, 150), or hæmatoxylin (Meyer, B. 12, 1392) with caustic potash. According to Hofmann (B. 11, 333) its dimethyl ether occurs in beechwood-tar creosote.

Preparation.—Pyrogallol is always prepared by heating gallic acid. In certain cases, as in the preparation of galleïn (Gürke, Germ. Pat. 30648, of Aug. 27, 1884; 32830, of Mar. 5, 1885) and anthragallol (Seuberlich, B. 10, 38) where high temperatures are employed, gallic acid is used and the decomposition into pyrogallol and carbon dioxide then takes place *in situ*.

On the large scale, gallic acid is heated with 2–3 times its weight of water in a bronze digester at 200–210° for about half an hour, the escape of the carbon dioxide evolved in the decomposition being provided for. The resulting almost colourless solution of pyrogallol is then boiled with animal charcoal, filtered, and rapidly evaporated, and the pyrogallol which crystallises out is finally distilled under a pressure of 20–30 mm. in order to obtain it in a pure and colourless condition. The yield is almost theoretical (Luynes and Esperandieu, C. R. 61, 489).

Other methods have been proposed (*cf.* Liebig, A. 101, 48; De Montlaur, Monit. Sci. 10, 1338), and in order to obtain the acid cheaply for photographic purposes, Thorpe (C. N. 43, 109) recommends that 10 grms. of gallic acid and 30 grms. of glycerine be heated at 190–200° as long as carbon dioxide is evolved. A theoretical yield is obtained, and the melt dissolved in a litre of water gives a solution suitable for dry-plate work.

Properties.—Pyrogallol forms white lustrous needles or thin plates, melts at 131° (Etti, B. 11, 1882), boils at 210° with partial decomposition (Pelouze, *l.c.*), has a bitter taste and is poisonous (Personne, C. R. 69, 749). It is readily soluble in ether, alcohol, and water, dissolving in $2\frac{1}{4}$ parts of water at 13° (Braconnot, *l.c.*), and its alkaline solution rapidly becomes brown and black on exposure to the air owing to absorption of oxygen, and then contains carbonic acid, acetic acid, black humus-like substances, and a little carbon monoxide. Gold, silver, and mercury salts are rapidly reduced by pyrogallol; a solution of a ferrous salt, free from any trace of ferric salt, produces a white turbidity in an aqueous solution of pyrogallol, but if any ferric salt be present a blue colouration is at once formed, which rapidly changes to a brown-red, owing to the oxidation of the pyrogallol by the ferric salt to a product yielding a blue colour with ferrous salts (Jacquemin, C. R. 77, 593).

Reactions.—Ferric salts in excess and other oxidising agents, such as potassium permanganate and chromic acid, oxidise pyrogallol to *purpurogallin* (Wichelhaus, B. 5, 848), a red compound which yields *naphthalene* on distillation with zinc-dust (Nietzki and Steinmann, B. 20, 1279).

Nitric acid oxidises pyrogallol to carbon dioxide and oxalic acid, and nitrous acid gives a brown colour to its aqueous solution, but when passed through its ethereal solution converts it into *nitropyrogallol* (Barth, M. 1, 882).

When heated with phthalic anhydride it yields *galleïn* (Baeyer, B. 4, 457, 555, 663; Buchka, B. 14, 1326), and with phthalic anhydride and a condensation agent, such as excess of sulphuric acid, it yields *anthragallol* (Seuberlich, B. 10, 42; *v.* Alizarin and allied colouring matters).

Uses.—An alkaline solution of pyrogallol is employed in gas analysis for the purpose of absorbing oxygen, 1 grm. of pyrogallol dissolved in aqueous potash being capable of absorbing 189·8 c.c. of oxygen (Liebig, A. 77, 107). Oxygen is most rapidly absorbed by a solution of 0·25 grm. of pyrogallol in 10 c.c. of either aqueous potash of sp.gr. = 1·050 (Weyl and Zeitler, A. 205, 264) or aqueous soda of sp.gr. = 1·030 (Weyl and Goth, B. 14, 2666). It must be noted, however, that carbon monoxide is always given off during the absorption, the amount evolved (calculated on the quantity of oxygen absorbed) being 2–4 p.c. with air or oxygen according to Calvert (C. R. 57, 873), 3·5 p.c. with oxygen, and 2·5 p.c. with air, according to Cloëz (C. R. 57, 875), and 0·4–3·4 p.c. with oxygen according to Boussingault (C. R. 57, 886). Both Cloëz and Boussingault agree in stating that the evolution of carbon monoxide is greater with pure oxygen than with mixtures of oxygen and nitrogen.

On the employment of pyrogallol as a developer in photography *v.* Photography.

Derivative.—The dimethyl derivative (*pyrogallol dimethyl ether*) $OH.C_6H_3(OMe)_2$ occurs in beechwood-tar creosote, and can be isolated by treating the fraction boiling at 250–270° with benzoic chloride, and subsequently decomposing the crystalline benzoyl compound (m.p. = 118°) with alkali (Hofmann, B. 11, 333; 12, 1373).

Properties.—It forms white prisms, melts at 52°, and boils at 253°. When oxidised with nitric acid, ferric chloride, chlorine, or preferably with chromic acid in acetic acid solution it yields *cedriret* (Hofmann, B. 11, 335; 12, 1371), whilst when mixed with the dimethyl ether of methylpyrogallol (also a constituent of beechwood-tar creosote) and caustic soda and oxidised by heating at 200° in the air it yields *pittical* or *eupitonnic acid*, which dyes silk orange in an acid bath, but has no value as a dye (Hofmann, B. 11, 1455; 12, 1377, 2216; *cf.* Grätzel, W. J. 1877, 940; Gottheil, Germ. Pat. 9328, of Dec. 31, 1878, expired May 1883).

Hydroxyquinol *Hydroxyhydroquinone* $C_6H_3(OH)_3[(OH)_3 = 1:2:4]$.

Preparation.—Hydroxyquinol is obtained, together with diquinol and δ-hexahydroxydiphenyl, by very rapidly heating hydroquinone with 8–10 times its weight of caustic soda until the evolution of hydrogen has almost ceased (Barth and Schreder, M. 4, 176; 5, 590).

Properties.—It crystallises from ether in microscopic scales, melts at 140°, and distils with partial decomposition into quinol. Its aqueous solution becomes rapidly coloured on exposure to the air, and when treated with a drop or two of dilute aqueous ferric chloride gives a transient bluish-green colouration, which, on addition of a very small quantity of aqueous sodium carbonate, becomes dark-blue, and, on the addition of more, wine-red.

Phloroglucinol, $C_6H_3(OH)_3[(OH)_3=1:3:5]$.

Formation.—Phloroglucinol is obtained by fusing certain glucosides, resins, &c., with caustic potash, as for example, phloretin, whence its name (Hlasiwetz, A. 96, 120), quercitrin obtained from species of *Quercus* (Hlasiwetz, A. 112, 98); maclurin, which in an impure form is obtained as refuse in the preparation of fustic (Hlasiwetz and Pfaundler, A. 127, 357: Benedikt, A. 185, 114), catechin, kino (Hlasiwetz, A. 134, 119, 122); dragon's blood (Hlasiwetz and Barth, A. 134, 283), gamboge (Hlasiwetz and Barth, A. 138, 68), and scoparin, a yellow dye obtained from *Spartium scoparum* (Hlasiwetz, A. 138, 190).

It is also obtained by fusing benzenetrisulphonic acid or phenol (Barth or Schreder, B. 12, 422), resorcinol (*ibid.* B. 12, 503), orcinol (*ibid.* M. 3, 649), with an excess of caustic soda. It has been prepared synthetically from ethyl malonate by Baeyer (B. 18, 3454).

Preparation.—It is best prepared by fusing resorcinol for about twenty-five minutes with 6 parts of caustic soda at a gradually increasing temperature until the vigorous evolution of gas, which soon sets in, almost ceases and the mass becomes a bright chocolate colour. The melt is then dissolved in water and the solution acidified with dilute sulphuric acid, filtered, and extracted with ether; the ether being subsequently almost completely distilled off, and the phloroglucinol which separates as a magma recrystallised after purification with charcoal (Barth and Schreder, *l.c.*). The product usually contains some resorcinol, which can readily be removed by heating it at 100°, and moistening with water from time to time until all the resorcinol has sublimed (Tiemann and Will, B. 14, 954).

Phloroglucinol can be completely freed from resorcinol and diresorcin by boiling with a concentrated aqueous solution of potassium hydrogen carbonate (bicarbonate). Under these conditions the potassium salt of phloroglucinolcarboxylic acid is formed which crystallises in needles, is sparingly soluble in a solution of potassium carbonate and alcohol, and when introduced into dilute hydrochloric acid gives the acid, which can be extracted with ether. The crystalline acid obtained by evaporation of the ethereal solution eliminates carbon dioxide when boiled with water, pure phloroglucinol remaining in solution (Will and Albrecht, B. 17, 2103; Will, B. 18, 1323; Skraup, M. 10, 721).

Properties.—It crystallises from water with $2H_2O$ in colourless tables and from ether in large rhombic tables (Will, B. 20, 298). These lose their water of crystallisation at 100°, forming the anhydrous compound which melts at 217–219° when rapidly, and at 200–209° when slowly, heated (Baeyer, B. 19, 2186). It sublimes without decomposition, has a sweet taste, reduces Fehling's solution, is readily soluble in water, alcohol, and ether, and, according to Tiemann and Will (*l.c.*), is more readily extracted from a neutral than from an acid aqueous solution. Its alkaline solution absorbs oxygen from the air, but less readily than pyrogallol (Weyl and Goth, B. 14, 2673), and its aqueous solution is coloured bluish-violet by ferric chloride. Unlike other hydroxybenzenes it yields an *oxime* on treatment with hydroxylamine (Baeyer, B. 19, 159), and in many of its reactions would seem to have the constitution of a triketone (*cf.* Baeyer, B. 18, 3454, and *l.c.*).

Detection.—When potassium nitrite is added to a very dilute solution of phloroglucinol and aniline nitrate, a cinnabar-red precipitate of benzeneazophloroglucinol is formed after a short time (Weselsky, B. 8, 967; Weselsky and Benedikt, B. 12, 226), a distinct precipitate being obtained at the end of three hours with only 0·0005 grms. of the substance. A similar reaction is, however, produced by maclurin, decoction of fustic, catechin, and extract of hops (Weselsky, B. 9, 217).

Phloroglucinol in the presence of hydrochloric acid gives a red-violet colour with woody substance, thus a solution containing 0·01 p.c. of phloroglucinol colours pine shavings moistened with hydrochloric acid a distinct red, and a solution containing no more than 0·001 p.c. will give the reaction if the shavings are allowed to remain in the solution for twenty-four hours (Wiesner, D. P. J. 227, 397; Kielmeyer, D. P. J. 227, 584; Wagner, D. P. J. 228, 173). The colour-reaction, however, is not afforded by cellulose which has been treated with caustic soda and bleached.

Two trihydroxybenzenes, œnoglucinol and phenoglucinol, have been described by Gautier (Bl. 33, 584). Both have the composition $C_6H_3(OH)_3+2H_2O$, and resemble phloroglucinol, with which they are not improbably identical, in properties.

Phenols $C_7H_5(OH)_3$.

Methylpyrogallol $MeC_6H_2(OH)_3$.

Occurrence.—It occurs as its dimethyl ether together with the dimethyl ethers of pyrogallol and propylpyrogallol in the fraction of beechwood-tar creosote which dissolves in alkalis and boils at 255–270°. (For method of separation v. Hofmann, B. 12, 1373.) The ether is hydrolysed by heating with hydrochloric acid at 160° for some hours. Methylpyrogallol melts at 129° and sublimes at higher temperatures. Its alkaline solution rapidly becomes brown in the air, and gives a blue colour with ferrous sulphate, thus resembling pyrogallol.

Phenols $C_9H_9(OH)_3$.

Propylpyrogallol occurs as the dimethyl salt picamar (Reichenbach, A. 8, 224; Niederist, M. 4, 489), in the fraction of beechwood-tar creosote boiling at 285°, from which it can be obtained by heating with hydrochloric acid at 130° (Hofmann, B. 8, 67; 11, 329; Pastrovich, M. 4, 184).

IV. Polyhydric Phenols.

1:2:4:5-Tetrahydroxybenzene (Nietzki and Schmidt, B. 21, 2378).

1:3:4:5-Tetrahydroxybenzene *Hydroxypyrogallol.* The dimethyl ether is obtained by reduction of dimethoxyquinone resulting from the oxidation of propylpyrogallol dimethyl ether (Hofmann, B. 8, 67; 11, 332) or trimethylpyrogallol (Will, B. 21, 602, 2020).

1:2:3:4-Tetrahydroxybenzene, *Apionol.* The dimethyl ether is obtained by heating apiolic acid with alcoholic potash (Ciamician and Silber, B. 22, 119, 2481).

Hexahydroxybenzene (Nietzki and Benckiser, B. 18, 505, 1836). W. P. W.

PHENOL COLOURING MATTERS. *Liebermann's Phenol Dyes. Weselsky's Dyes. Dichroïns.* V. OXAZINE COLOURING MATTERS.

PHENOLPHTHALEÏN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHENOPHENANTHRAZINE *v.* AZINES.

PHENOSAFFRANINE *v.* AZINES.

PHENYL BROWN, *Phénicienne*, is a yellowish-brown powder which explodes on heating, and consists of dinitrophenol and an amorphous brown substance (Bolley, W. J. 1869, 585). It is obtained by gradually adding 10 to 12 parts of a mixture of 2 volumes of sulphuric acid and 1 volume of nitric acid (sp.gr. = 1·35) to 1 part of well-cooled phenol until red fumes are no longer evolved; the product is then poured into water, and the precipitated dye filtered off and washed (W. J. 1865, 613). It dyes wool and silk without a mordant, giving brown shades which are fast to light; but it is now seldom, if ever, employed in dyeing.

PHENYLENE BLUE *v.* INDAMINES AND INDOPHENOLS.

PHENYLENE BROWN *v.* AZO- COLOURING MATTERS.

PHENYLENE DIAMINES *v.* DIAMINES.

PHENYLENE VIOLET *v.* INDAMINES AND INDOPHENOLS.

PHENYLHYDRAZINE *v.* HYDRAZINES.

PHENYLHYDRAZINE ACETYL $(C_6H_5)HN.NH(CO.CH_3)$, or **Pyrodine**, first synthesised by A. S. Leibmann, has been therapeutically examined by Dreschfeld (S. C. I. 1888, 765), who drew attention to the toxic action of the drug. Lepin has since confirmed this latter observation (Lyon médic. 1888, No. 80). Merck, however, observed that the toxic action is due to the fact that, as hitherto prepared, the substance is of variable nature, and that the poisonous properties are due to impurities (Merck's Bull. 2, 13–20; S. C. I. 8, 476).

PHILLIPIUM *v.* CERIUM METALS.

PHLORIDZIN *v.* GLUCOSIDES.

PHLOROGLUCIN *v.* GUM RESINS.

PHLOROGLUCINOL *v.* PHENOL AND ITS HOMOLOGUES.

PHLOROL. A name given to ortho-ethylphenol, on account of its formation from phloretic acid by distillation with lime (Oliveri, G. 13, 264).

PHLOROSE *v* DEXTROSE.

PHLOSCEÏNE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHLOXINE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHOCENIC ACID. A name given by Chevreul to isovaleric acid (*v.* FATTY ACIDS).

PHŒNICITE. *Basic lead chromate* (*v.* CHROMIUM).

PHŒRETIN *v.* RHUBARB.

PHOSGENE GAS. J. Davy's name for carbonyl dichloride or carbon oxychloride (*q. v.*).

PHOSGENITE. A chloro-carbonate of lead $PbCl_2.PbCO_3$, *v.* LEAD.

PHOSPHINE. A syn. for phosphoretted hydrogen PH_3, *v.* PHOSPHORUS. Used also to designate the nitrate of chrysaniline or diamidophenylacridine $C_{19}H_{15}N_3.HNO_3$, *v.* CHRYSANILINE.

PHOSPHOMOLYBDIC ACID *v.* MOLYBDENUM.

PHOSPHOR BRONZE *v.* TIN.

PHOSPHORITE *v.* CALCIUM; also MANURES.

PHOSPHORUS. Sym. P. At.w. 30·96. Vapour density = 61·92. From φῶς, light; and φέρω, I bear. Phosphorus was accidentally discovered by an alchemist named Brandt, of Hamburg, while experimenting with urine, in the year 1669. As urine contains only a minute quantity of phosphoric acid,[1] phosphorus was not generally known till about 100 years after, when Gahn in 1769 showed it to be an essential constituent of bones, and Scheele, taking advantage of this discovery, made phosphorus from bone ash.[2] It is stated 'that Brandt by a secret process[3] succeeded in preparing phosphorus from urine, and he is said to have sold the secret of the manufacture to Krafft, from whom it appears that Kunkel learnt what he knew, and published in the year 1678 a pamphlet on this remarkable product. In those early days phosphorus was a very costly body, being valued as one of the most remarkable and interesting of chemical substances.

'Krafft exhibited it as one of the wonders of nature to various crowned heads, among others, in the year 1677, to King Charles II. of England.'[4]

From the fact of the presence of phosphorus in bones, its universal diffusion in nature might have been suspected. Nevertheless, it has only of late been demonstrated how widespread are the compounds of phosphorus. In fact, upon a soil free from phosphorus no plant could grow, as its presence is essential to the formation of the plant structure, and is found in largest quantities in the seed and fruit. Phosphorus, likewise, is necessary for the growth and nutrition of the animal tissues, and is present both in the substance of the brain and in the nervous matter connected therewith. It ranks, therefore, like oxygen, nitrogen, hydrogen, carbon, &c., as one of the elements necessary to the building up of the animal and vegetable body. Besides being present in all fruitful soils, phosphorus is present in most springs, in all rivers, in the sea

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[1] 1450 c.c. of urine contains, alkaline phosphates 2·1 grms., earthy phosphates 1·3 grms. (Ralfe's Clinical Chemistry, p. 105). [The above is equivalent to about ·032 p.c. of phosphorus in urine.]

[2] See report by Juries of International Exhibition, London, 1862, p. 93.

[3] The process consisted in distilling evaporated urine with sand in clay retorts.

[4] Roscoe and Schorlemmer, Treatise on Chemistry, vol. 1, p. 458.

(J. pr. 34, 185; B. J. 26, 393), and even, it is stated, in minute traces in the atmosphere (Barral). At one time phosphorus was considered to be a compound body containing 'phlogiston' and an acid, till Lavoisier investigated the subject in the year 1780, and showed that when phosphorus is burnt in air the acid produced weighed more than the phosphorus itself, the increase in weight being due to the oxygen of the atmosphere with which the phosphorus had combined (Opuscules Physiques et Chimiques, 1774).

Up to the year 1845 the 'yellow' or ordinary crystalline phosphorus was the only variety known. Since then an allotropic modification has been recognised, and is now extensively used in commerce under the name of 'red' or 'amorphous' phosphorus. This form differs from the crystalline phosphorus in most important properties, in a degree almost as great as do the allotropic modifications of carbon or sulphur among themselves. Amorphous phosphorus was discovered by Schrötter in 1845, although its existence had been previously observed by other chemists, who had misunderstood its nature. Other modifications of phosphorus are said to exist; these will be referred to when discussing the general properties of phosphorus. Scheele's method of producing phosphorus, first published in 'Gazette Salutaire de Bouillon' in the year 1775, consisted in dissolving bone ash in nitric acid, and then removing the lime as sulphate with sulphuric acid; but this method was afterwards simplified by Nicholas and Pelletier, who decomposed the bone ash direct with sulphuric acid, and further improved by Fourcroy and Vauquelin, who determined the exact quantity of sulphuric acid required for the complete decomposition of bone ash. The last method is that still used in the manufacture of phosphorus.

THE MANUFACTURE OF PHOSPHORUS.

(*a*) *The Raw Materials.—Phosphates.* Of all the phosphates now to be had in the market pure bone ash is to be preferred, other things being equal, over the others for the manufacture of phosphorus, inasmuch as it contains a high percentage of phosphate of lime; it is easily decomposed by sulphuric acid; and it contains only small quantities of magnesia, oxide of iron, and silicious matter.

On the other hand, it has to be considered that bone ash probably costs more to-day, per unit, than any other phosphate of lime.

Pure bone ash (from ox-bone) possesses the following composition:—

	Per cent.
Phosphoric acid (P_2O_5) [1]	39·55
Lime	52·46
Magnesia	1·02
Oxide of iron	0·17
Carbon dioxide, alkalis, &c.	4·43
Water, carbonaceous matter, &c.	0·86
Silicious matter	0·51
	99·00

Bone ash, as met with in commerce, varies considerably in composition, the amount of phosphoric acid existing as tri-calcium phosphate varying between 27 and 37 p.c. It is chiefly imported from South America, and is not obtained entirely from bones, but contains in addition the ash of other parts of the carcase. Subjoined is an analysis of commercial bone ash:—

Bone ash from South America.

	Per cent.
Phosphoric acid (P_2O_5) [1]	33·68
Lime	43·37
Magnesia	1·14
Oxide of iron	·58
Carbonic acid	4·22
Alkalis	·62
Water, carbonaceous matter, &c.	6·70
Silicious matter	9·69
	100·00

Another very suitable phosphate of lime, which is to be had in small quantities, is what is known as precipitated phosphate of lime. This substance is obtained as a by-product in the manufacture of glue from bones. The method adopted is a modification of the system proposed by Fleck (Wagner's Chemical Technology, p. 543). The bones, previously crushed and deprived by boiling of the fat they contain, are soaked in a weak solution of hydrochloric acid, until they become quite soft. The clear liquor, containing the phosphate of lime in solution, is drawn off from the cartilaginous substance, and milk of lime is cautiously added to it, in quantity sufficient to throw down the phosphates, which are then washed, dried, and collected. The following analysis of a quantity of this phosphate which was used in the manufacture of phosphorus will show what a very rich phosphate is obtained in this way:—

Precipitated Phosphate of Lime.

	Per cent.
Phosphoric acid (P_2O_5) [2]	39·45
Lime	44·88

This phosphate dissolves easily and gives an excellent phosphoric acid.

The next raw material to be referred to as a source of phosphorus is apatite. Apatite is a pure form of mineral phosphate of lime, combined with either calcium fluoride or calcium chloride forming the definite chemical compounds *Fluor apatite* ($3Ca_32PO_4.CaF_2$) or *Chlor apatite* ($3Ca_32PO_4.CaCl_2$). The pure crystals of the former contain 42·26 p.c. phosphoric anhydride, while the crystals of the latter contain 40·92 p.c. This last variety is not so largely imported. Fluor apatite comes from Canada, and also from Spain under the name of Spanish phosphorite. The Canadian phosphates are frequently highly crystalline and of a light green or red colour. They are found in the Ottawa district of Canada, in the volcanic rocks of New Jersey and New York, and other places in the American continent. They contain neither organic nodules nor fossils, as many other phosphates do, but have the phosphoric acid evenly distributed through large masses of the rock. The following analyses of two lots of Canadian phosphates will give some indication of the general composition:—

---

[1] Equal to 17·26 p.c. phosphorus.

[1] Equal to 14·70 p.c. of phosphorus.

[2] Equal to 17·20 p.c. of phosphorus.

Canadian Phosphate of Lime.

	Per cent.	Per cent.
Phosphoric acid (P_2O_5) .	33·51[1]	37·68[2]
Lime	46·14	51·04
Oxide of iron, Alumina, Fluorine, &c. . . .	7·83	6·88
Silicious matter . .	11·90	4·29
Water and loss on ignition	·62	0·11
	100·00	100·00

The absence of carbonates makes the complete decomposition of this phosphate with sulphuric acid troublesome and tedious when operating on large quantities.

The Spanish variety of apatite, called also *Estramadurite*, has the following percentage composition:—

Spanish Phosphorite (Voelker).

	Per cent.
Phosphoric acid[3]	33·38
Lime	47·16
Magnesia	trace
Carbonic acid	4·10
Sulphuric acid	·57
Oxide of iron	2·59
Alumina	·89
Fluorine and Iron . . .	4·01
Silicious matter . . .	3·71
Water	3·59
	100·00

Another phosphate used in the manufacture of phosphorus and found very suitable, both on account of its comparative freedom from iron and the presence of a certain amount of carbonates, is 'Sombrero phosphate,' obtained from the small uninhabited island of that name in the Caribbean Sea. It contains the following:—

Sombrero Phosphate.

	Per cent.
Phosphoric acid[4]	35·12
Lime	51·33
Iron and alumina . . .	1·02
Carbonic acid	7·40
Silica	2·02
Alkaline salts	·42
Water and loss on ignition .	2·69
	100·00

French phosphates contain from 50 to 75 p.c. of phosphate of lime. The high-class qualities should be found useful in this manufacture. The next phosphate to be referred to is 'Redonda phosphate,' both on account of its high percentage of phosphoric acid, its low price, and also from the fact that this peculiar mineral has been the subject of many patents having for their object the utilisation of the phosphoric acid it contains. Redonda phosphate, like Sombrero phosphate, comes from the West Indies; it contains no lime, the phosphoric acid present being combined with iron and alumina.

Redonda Phosphates.

	I.[1]	II. (Readman)
Phosphoric acid .	35·47[2]	39·71[3]
Oxide of iron . .	8·85	9·45
Alumina . . .	20·17	20·90
Silicious matter .	9·70	6·65
Organic matter, and water of comb. .	7·20	22·86
Moisture . . .	18·61	
	100·00	99·57

The processes proposed for working this phosphate will be referred to subsequently. The last mineral phosphate to be mentioned in connection with this part of the subject is what is known in the market as Charleston phosphate. This is not a high-class phosphate, like some of those considered, nor is it very free from iron and alumina, but it has the property of being easily and uniformly decomposed when treated with sulphuric acid, and is of very regular composition. Charleston phosphate is found in the beds of several of the rivers and on the lands of South Carolina. The river phosphate differs slightly from that of the land both in colour and hardness; moreover, in the river phosphate the iron exists partly as pyrites, while in the land phosphate it exists as ferric oxide. The river variety is that usually sent to this country, being richer in phosphates. It is obtained by dredging the river, and is dried by hot air before exportation.

Charleston Phosphate (Readman).

	Per cent.
Phosphoric acid (P_2O_5)[4] . .	27·17
Sulphuric acid	3·30
Carbonic acid	4·96
Lime	44·03
Magnesia	0·37
Alumina	1·44
Oxide of iron	0·43
Bisulphide of iron . . .	3·60
Alkaline salts	0·87
Fluorine, &c.	2·38
Combined water and loss on ignition	4·60
Sand	5·60
Moisture	1·25
	100·00

This enumeration does not by any means exhaust the various phosphates available for the production of phosphorus; but the list here given of crude materials which are, or which may be, employed in the manufacture, will convey an idea of the resources at the disposal of phosphorus makers.

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[1] Equal to 14·63 p.c. of phosphorus.
[2] Equal to 16·45 p.c. of phosphorus.
[3] Equal to 14·57 p.c. of phosphorus.
[4] Equal to 15·33 p.c. of phosphorus.

[1] C. N., June 18, 1875.
[2] Equal to 15·49 p.c. of phosphorus.
[3] Equal to 17·33 p.c. of phosphorus.
[4] Equal to 11·86 p.c. of phosphorus.

It may be added, that whichever variety of phosphatic material be employed, it is absolutely essential to reduce it to a very fine state of division as a preliminary step in the manufacture of phosphorus.

Further, it must be remembered that the presence of iron, alumina, magnesia, and alkalis—as also any *excessive* amount of carbonates—is objectionable. The former substances are dissolved, to a great extent, during the sulphuric acid treatment, and reappear at a later stage, in the phosphorus retorts, while carbonates, of course, consume their equivalent quantity of sulphuric acid, and thus add to the cost of production.

As has been indicated, however, a certain limited quantity of carbonate of lime is advantageous in the sulphuric acid treatment, as it materially assists the decomposition of the phosphatic material operated upon.

The amount of carbonate of lime should not exceed, say, 10 to 12 p.c. for economical work.

Generally speaking, a high-class phosphate should be selected—one containing at least 70 p.c. of phosphate of lime. Such phosphates are now easily obtained in the market, and the advantages of employing them are very great.

With respect to the other material used in the manufacture of phosphorus (at least in the initial stage)—namely, sulphuric acid—it will suffice to say that ordinary chamber vitriol of sp.gr. 1·500 to 1·600, free from arsenic, is quite suitable for decomposing the phosphate of lime into sulphate of lime and phosphoric acid.

(*b*) *The preparation of phosphoric acid.* In this, as in subsequent processes, the author will describe the plant (alluding incidentally to noteworthy matters) which, from personal practical experience, he has found to yield good results.

The decomposition of phosphate of lime by sulphuric acid is performed in a circular wooden vessel, shaped like a brewer's mash tun, 10 feet in diameter and 8 feet deep, provided with an upright wooden agitating shaft carrying three arms placed at regular intervals between the bottom and middle of the vessel.

The only ironwork in the interior of the decomposing vessel consists of a cast-iron shod on the lower extremity of the revolving shaft, and a strong cast footstep in which it works. The revolving arms are simply tenoned into the upright shaft. Pitch pine 3 inches thick, is preferably employed in the construction of the decomposer, and before use the tun is thoroughly saturated with light tar-oil, which acts as a preservative and keeps the vessel in good repair for many years. It is securely bound by strong hoop iron, which may with advantage be protected by sheet lead at any part exposed to the drip of acid. The agitator is driven by a crown wheel and pinion, connected in the usual way with a steam engine. At the lower circumference of the tun, as near the bottom as possible, a wooden man-hole door is provided, and this, opening outwards, allows the charge to be run out to the adjoining filters.

The operation of decomposing the phosphate of lime is thus conducted. The tun is filled to the depth of about 18 inches with weak liquors from a previous decomposition, and to this is added about 2 cwts. of phosphate of lime. High pressure steam is then blown in by a lead pipe, until the liquor boils, when the steam is shut off. The agitator is now put in motion, and charging is commenced, adding alternately, say, 6 cwts. of finely-ground phosphate, and 5 carboys of chamber sulphuric acid (sp.gr. 1·500 to 1·600), till the whole has been introduced. A convenient charge for such a decomposer as has been described is from 80 cwts. to 100 cwts. of phosphate, and the equivalent quantity of sulphuric acid necessary to decompose into sulphate the *total lime present*, existing either as carbonate or as phosphate of lime,[1] thus:

$$Ca_3 2PO_4 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

It is advisable not to introduce the charge too rapidly, but rather to allow ample time for a uniform decomposition to take place. The charging should be completed in three hours, and it is well to continue the agitation an hour, or even more, until all visible action has ceased.

When it is ascertained that the decomposition is complete, the large man-hole door is gradually opened, and the entire contents of the tun run off by a shoot to one of a series of filters, conveniently arranged below the level of the decomposer, agitation being still maintained.

The filters are rectangular wooden tanks, each about 20 feet long, 16 feet wide, and 2½ feet deep. They are not set level, but are laterally inclined at a gradient of about 1 in 30, so as to drain towards ten exit holes pierced along the lower side. The filtering medium consists of ashes. Coarse 'clinkers' are spread evenly over the floor, and a layer of sieved ashes above, the entire depth of the filtering bed being about 6 inches.

The filtering tanks are securely bound with tie rods, and before use the wood-work is impregnated with light tar-oil. As it drains from the filters, the phosphoric acid liquor is caught in a wooden launder, common to the series of outlets on the filter tanks, and is conveyed by it to wooden lead-lined tanks in which strong liquors and weak washings are kept apart.

The strength of the solution at first draining from the filters is about 30°Twad. (sp.gr. 1·150). The flow must not be allowed to proceed too rapidly, as the bed of gypsum or 'sludge' in the filters if allowed to dry will crack on the surface, and a very imperfect washing will be the result. A spray of water is run over the gypsum by a perforated pipe running along the higher side of the filter tanks. This spray is so regulated as to keep the sludge covered with one or two inches of water until the end of the operation. The upper surface of the gypsum is carefully raked every few hours with a wooden mud-rake, so as to fill up any cracks through which the washing water might find too ready an exit. The spray is continued until the effluent washings are 2°Twad. (sp.gr. 1·010). The water is then turned off, and the sludge is allowed to dry, being finally piled up to permit the last trace of washings to drain from it. The gypsum is then removed from the filter tank to undergo artificial desiccation.

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[1] This statement differs from that given in most of the text books on Chemistry, which state that sulphuric acid is added in quantity only sufficient to form the acid phosphate of lime, thus:—

$$Ca_3 2PO_4 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

Four samples of wet gypsum sludge, as removed from the filters, gave the following analyses:—

Partial analyses of four samples of sulphate of lime from the filters	Per cent.			
	I.[1]	II.	III.	IV.
Water and loss at a red heat	49·2	63·2	63·0	64·6
Total phosphate of lime in wet sludge . .	3·6	0·3	0·39	0·13
Phosphate of lime, calculated on dry . . .	7·08	0·83	1·03	0·36

[1] No. 1 shows imperfect washing.

The phosphoric acid draining from the filters is considered 'strong liquor' until it falls below 10°Twad. (sp.gr. 1·050), and this first fraction is reserved for concentration. The latter fraction, between 10°Twad. and 2°Twad. (sp.gr. 1·050 and 1·010), is employed partly for the decomposition of a further lot of phosphate, as has been described, and partly for the first washing upon the filter before the water spray is turned on. Both fractions are blown by means of Körting's or other elevator, such as an 'acid egg,' to stock tanks, from which the evaporating vessels, and the decomposer or filters, can respectively be supplied by gravitation.

(*c*) *Utilisation of the gypsum sludge.* The wet sludge removed from the filters contains water, phosphoric acid, and undecomposed phosphate of lime in quantities varying according to the care bestowed on the operations described. The sludge may be dried upon a bed formed of fireclay-covers over flues heated by any available waste heat. When sufficiently dry, the gypsum is passed through a sieve to break up the larger lumps, and is in this state sold to manure makers as a dryer for superphosphates; or it is used to fix the ammonia in the compost heaps of the farmer, and for other purposes. The following is the analysis of a quantity of dried gypsum made in the way described:—

	Per cent.
Lime	31·80
Sulphuric acid	44·93
Soluble phosphoric acid . .	0·50
Insoluble phosphoric acid. .	2·57
Oxide of iron and alumina .	2·20
Silicious matter	12·10
Organic matter	1·20
Combined water	4·15
Moisture	0·50
	99·95

The gypsum during the process of drying should be occasionally turned, to expose fresh surface to the heated bed.

(*d*) *Concentration of phosphoric acid liquor from the filters.* This may be accomplished either in shallow rectangular wooden tanks, lined with 10 lb. lead, and provided with lead pipes (1½ inch diameter, and 20 lbs. lead to 1 foot) through which high-pressure steam is allowed to pass; or it may be performed in a cast-iron saucer-shaped pan, also lined with lead and having steam coils as before. During evaporation the liquor is maintained in motion by an agitator, provided with arms, and driven as usual by power. The latter system is the one to be preferred. Agitation of the liquor during concentration, besides hastening the evaporation, prevents the accumulation of gypsum on the steam coils, a result which invariably occurs in any unstirred evaporator. Such deposit, if allowed to form, becomes extremely hard and difficult to remove without injury to the lead pipes.

The stronger phosphoric acid from the filters —that above 10°Twad.—is allowed to flow by gravitation from the stock tank to the evaporator, to be concentrated till the clear yellow-coloured phosphoric acid attains a strength of from 65°T. to 100°T. (sp.gr. 1·325 to 1·500), according—as will be immediately explained—to the selected method of subsequent treatment. During the evaporation nearly all the sulphate of lime held in solution is precipitated, so that the concentrated acid liquor retains only a very small quantity of lime. Almost all of this lime ultimately deposits as sulphate after settling in the stock tank. As the phosphoric acid liquor becomes more and more concentrated, some of the free sulphuric acid which may be present is expelled during the evaporation—the steam or vapour from the evaporator having frequently a strong acid reaction. The following are some analyses of phosphoric acid liquors at various strengths made from phosphates which are not named:—

—	Strength				
	58°T.	69°T.	72°T.	86°T.	90°T.
Uncombined phosphoric acid (P_2O_5)	19·30	27·60	29·20	34·02	36·44
Combined phosphoric acid (P_2O_5) .	4·68	3·61	3·60	4·40	4·80
Sulphuric acid (SO_3) . . .	2·47	1·40	·70	—	1·39
Alumina and oxide of iron, &c. .	1·92	2·56	—	3·26	3·61
Lime	—	1·00	—	·84	trace
Water	71·63	63·83	66·50	57·48	53·76
	100·00	100·00	100·00	100·00	100·00

The gypsum deposited in the evaporators or in the stock tank may either be washed by itself on a small filter, or it may be removed to the large acid filter, and be washed along with the sludge from the decomposer. If conveniently situated, the latter is the more economical method.

The concentrated acid is cooled in lead-lined store tanks, where, as has been said, the last traces of sulphate of lime are deposited, and the acid is then ready for the next operation of mixing with carbon and drying.

(*e*) *Mixture for the retorts.* The concentrated phosphoric acid may now be mixed with coarsely-ground wood charcoal, coke, or sawdust, and carefully dried in a cast-iron pot or muffle furnace.

The author has used carbon in the latter form, and finds that some advantages are thereby secured. Sawdust absorbs a large quantity of liquor, so that when it is employed concentration of the acid liquor to the minimum sp.gr. of 1·320 is permissible, and, when thus saturated, it can be easily handled without loss through sweating.

On the other hand, the greater bulk, and the low specific-gravity, of sawdust present objectionable features. If sawdust be employed, the mixing may be accomplished on a clean brick or asphalt floor, and the wet charge can then be carefully charred in a well-built muffle furnace.

If coke or charcoal be used, the preliminary concentration of the phosphoric acid to a syrupy consistence is indispensable, and the mixing should be done in a cast-iron pot, in which the charge is subsequently dried by fire-heat from beneath. The amount of fixed carbon required is about 25 p.c. by weight of the concentrated acid liquor. Great care must be taken with the drying of the charge. The heat must be regular and not too high, and when it is completed the charred mass must be carefully preserved from air in malleable or cast-iron boxes provided with closely-fitting lids, and conveniently situated for the retorts. The following notes may be interesting:—

Experiments to ascertain the volatility of phosphoric acid during the charring of sawdust saturated with phosphoric acid[1]:—

Experiment I. 'A known quantity of phosphoric acid was mixed with twice its weight of dry sawdust and heated in an iron tube to a low red-heat. The products evolved were collected in nitrogen bulbs containing dilute nitric acid, but not the slightest trace of phosphoric acid could be detected in the contents of the bulbs.'

Experiment II. 'Used phosphoric acid liquor, 1·41 sp.gr. (82°T.), containing free phosphoric acid 22·75 p.c. 50 grains of above were mixed with 50 grains dry sawdust and heated in a covered porcelain crucible gradually till the sawdust was completely charred. The temperature was then raised to full redness, and was maintained at this for half an hour. Estimated the phosphoric acid and found *no loss.*'

(*f*) *The description of the clay retorts, their manufacture, and details of the clay employed.* The retorts in which the charred mixture is distilled are made of Stourbridge fireclay. The author has tried other clays, but found none so durable for the purpose as that from Stourbridge. The retorts are shaped much like a large bottle. The accompanying sectional sketch will show the appearance they present.

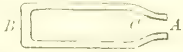

Fig. 1. Phosphorus Retort made of Stourbridge Clay.

The total length A to B is 3 feet. The internal diameter is about 8 inches. The clay is about 1 inch thick, except at B, where it is about 1½ inches. The neck is gradually tapered from C to A, where the internal diameter is 3 inches. Into this narrow orifice a 2-inch mal. iron pipe leading to the condenser is luted, and can be easily removed to empty and charge the retorts.

The retorts should be made at the phosphorus works; the clay employed is such as is used for glass-house pots, and is tolerably free from iron, rich in silica, and comparatively low in alumina. The clay, as generally supplied from Stourbridge, has previously undergone the operation of 'weathering' for many months. This renders it plastic, more easily worked, and much more durable when made into retorts. The following analyses of the clay, raw and calcined, have been supplied through the courtesy of a firm in Stourbridge:—

	Raw	Calcined
Silica	72·50	76·97
Alumina	18·65	19·97
Protoxide of iron . .	1·58	1·67
Lime	0·26	·28
Magnesia . . .	0·46	·49
Potash	0·33	·35
Soda	0·18	·19
Water and organic matter	5·78	none
	99·74	99·92

A mixture which has been successfully employed for the construction of retorts consists of two parts of the raw clay, finely ground, carefully mixed with one part of the calcined clay coarsely ground.

The mixture is allowed to 'sour' or season for three or four weeks by incorporating it with water to a thick doughy consistence, and leaving it piled up in a low flat heap, about 16 feet long and 3 feet in depth, after which it is ready for moulding into retorts. The apparatus required for the latter is not very elaborate. It consists of a turntable or wheel, upon which the retorts are built, and a sheet-iron mould about 3 feet long, divided into two lengths of about 18 inches each, with a fishing-rod joint to connect the one to the other.

On the turntable a loose base-piece of plank, about 12 inches square, is first placed, to support the mould containing the soft clay retort, during its removal to the drying room. Wooden beaters, and a flat circular disc, 6 inches in diameter, with a shaft, like an old-fashioned churn stirrer, are also required.

Before commencing to build a retort, the inside of the iron mould is smeared over with oil to prevent the clay adhering to the iron.

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[1] Report by Dr. Clark, Glasgow, to the author when he was engaged in the manufacture of phosphorus.

This done, the lower half of the sheet-iron mould (which is about 1 foot in diameter) is placed on the square board surmounting the turntable (a small quantity of sand having been first sprinkled over the board). The clay in a tough plastic state is introduced into the mould. This is worked by the hand to the shape of the bottom part of the retort. The clay is well beaten to the side with the wooden beater, and the bottom is pressed hard down by a circular disc. When the lower half of the retort is constructed in the way described, the upper portion of the iron mould is then jointed on, and this is likewise built up with clay in the same way till the whole retort is completed.

Some delicacy is required in making the tapered neck, but experienced workmen have little difficulty in doing this. The retort with the mould is now ready for removal to the stove-room, which should adjoin the retort house. The temperature in the heated room is maintained at 90°F. by means of flues below the floor. After remaining about a week in this room the retorts have shrunk sufficiently to admit of the moulds being withdrawn. When this is done, the outer skin of the retorts which was next the moulds has its hollows carefully filled up with damp clay. The retorts are then washed with a thin emulsion of clay and water until the outer surface is smooth and free from cracks or holes. They remain in this room for at least 3 weeks longer, or until they are required for use. Retorts with cracks or flaws are here rejected.

When starting a new bench of retorts, or when re-starting a furnace that has been off for repairs, the retorts may be taken direct from the stovehouse and placed in the cold furnace. The fire is lighted, and the heat gradually raised to the temperature necessary for the manufacture of phosphorus.

In actual work, however, it is a common experience to find two or three retorts in a furnace broken, and, in order to replace these without interruption of the usual work, it is necessary to take the required number of new retorts from the stove-house, and place them in a special kiln, to be slowly heated to the temperature of the working furnace which contains the broken retorts. When this temperature has been attained, the new retorts are quickly removed from the kiln and are placed in the working-furnace, the broken ones having of course been first removed.

(*g*) *The Phosphorus Furnace.* The furnace used in the distillation of phosphorus is of the galley type, similar to that employed in the distillation of zinc by the Belgian process. A convenient size holds twenty-four retorts, twelve on each side, arranged in two tiers—that is, six retorts on each tier. The retorts are placed back to back, their necks protruding slightly (1-inch) through the side walls of the furnace. The closed ends of the retorts are supported by a 9-inch wall, having fireclay covers built into it over the spaces into which the ends of the lower tier are inserted. This wall divides the furnace longitudinally. The furnace measures about 12 to 13 feet long and about 7 feet broad, outside dimensions. The firegrate is $5\frac{1}{2}$ feet in length by $1\frac{1}{2}$ feet in breadth, and the firebars are made of 2-inch square wrought-iron. Over the firegrate, about $2\frac{1}{2}$ feet above the bars, a $4\frac{1}{2}$-inch firebrick arch is thrown. This arch has six ports on each side, corresponding to the six retorts, and these are so placed that the fire ascends between each pair of retorts. The arch extends from end to end of the furnace. Upon the top of this arch the 9-inch wall previously mentioned is built. This wall is about 2 feet in height, and is sufficiently high to allow the ends of the upper tier of retorts to rest on the top of it, the ends of the lower tier resting on covers

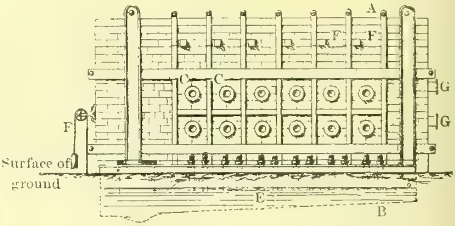

FIG. 2.—PHOSPHORUS FURNACE.

(Side elevation.)

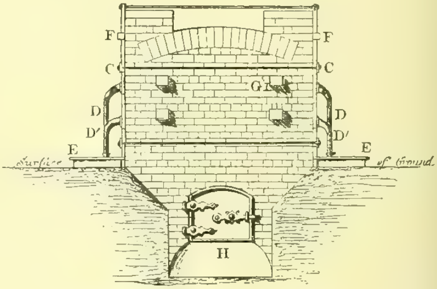

FIG. 3.—PHOSPHORUS FURNACE.

(Front elevation.)

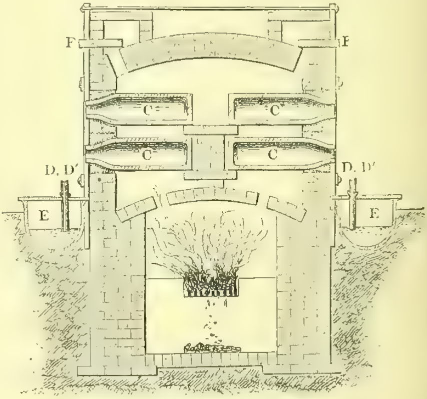

FIG. 4.—PHOSPHORUS FURNACE.

(Transverse section through A–B, Fig. 2.)

C. Phosphorus retorts. D, D'. Pipes to condenser. E. Condensing trough. F. Dampers. G. Spyholes. H. Fire door.

built into the wall about 6 inches above the arch which covers the fire. The outer walls of the furnace are 9 inches thick, and the outer arch which incloses the whole is also made of 9-inch firebrick. The retorts are, in fact, simply suspended in what is practically two flues in one furnace, the walls of which are the outer walls of the furnace and the 9-inch central dividing wall.

The furnace must be very firmly bound, both longitudinally and transversely. This is all the more required as the walls of the furnace must necessarily be thin, and, moreover, each retort has a 12-inch square port-hole through which it is primarily introduced into the furnace. All these circumstances, tending to weaken the side walls, point to the necessity of securely and substantially binding the furnace.

The preceding sketches (Figs. 2, 3, and 4) will show the general construction and arrangement of the furnaces and side condensing troughs.

The heat from the fire ascends through the ports on the 4½-inch arch described above, and passes through the chambers in which the 24 retorts are hung, and then it escapes through 6 ports on the upper 9-inch arch to small flues built on either side of the top of the furnace. The products of combustion now travel along these flues and descend at the back of the furnace furthest from the fire to the main flue. If required, this waste heat may be first utilised to dry the gypsum from the phosphoric acid filters. The firebricks used in the construction of the furnace must be of the very best description, and none but a most experienced furnace-builder should be entrusted with the erection of it. Dampers are placed on each of the upper port-holes, and a large damper where the 2 small flues unite with the main flue. Spyholes should be placed on the front wall of the furnace, so that the chambers containing the retorts can be conveniently viewed. This is a most important provision, and should in no case be neglected, as frequently retorts are cracked, and there is no other means so simple as the spyhole to ascertain their condition. When starting a new furnace great care must be taken not to raise the heat so rapidly as to cause cracks in the walls, which would admit cold air and be fatal to the retorts; and, when the necessary heat has been attained, as much caution is required to maintain a steady temperature. Clay retorts are very sensitive to sudden changes of temperature, and the life of a retort largely depends upon its treatment in this respect.

(*h*) *The Distillation.* The 24 retorts having been placed in the port-holes in the manner described, their necks are built in with broken bricks and fireclay to prevent access of air into the interior of the furnace. The fire is now lighted and the heat very gradually increased, care being taken during this time to have the dampers only slightly open. After 18–24 hours firing the retorts should be at a bright-red heat and ready for charging. This is performed by means of a scoop made out of a 2-inch malleable iron pipe, which has been opened up and provided with a handle. The scoop is about 18 inches long, and made so as to enter the 3-inch neck of the retort without difficulty.

The retorts hold conveniently about 20–30 lbs. of the charred mixture. It is advisable not to fill them more than two-thirds full. This does not take more than a few minutes to accomplish, and whenever it is done the 2-inch malleable iron pipe leading to the condenser should be at once luted on. Various forms of condensers may be employed. A suitable arrangement consists in having long troughs on each side of and close to the furnace (as shown in Figs. 2, 3, and 4) made of light cast-iron, about 12 feet in length by 18 inches broad by 24 inches deep at one end and 18 inches at the other end. The lip of these tanks has a 3-inch flange on outside, upon which the cast-iron cover is bolted. Twelve 3-inch cast-iron pipes with faucets pass through this cover, and dip an inch or two into the water with which the trough is partially filled. These short pipes are so placed that the 2-inch malleable iron pipes before referred to can be conveniently luted to their faucets, and thus connect the retorts with the condenser.

The water in these troughs soon becomes warm with the hot gases bubbling through it. This is advantageous, as it prevents solid phosphorus choking up the pipes. The bottom of the troughs being deeper at the one end than at the other causes the melted phosphorus to run down to the lower end, from which it can be removed from time to time by ladles.

The incondensable gases are removed from the trough by a 10-inch pipe, and can either be sent at once to the stalk or connected with further condensing arrangements. Care must be taken when charging the retorts to avoid spilling any of the charge into the condensing troughs, and to insure this it is well during the operation to employ sheet-iron trays which cover the open faucets.

The luting used for the 2-inch pipes, both at the retort and faucet ends, is fine ground fireclay, with salt, or with a small quantity of borax added to prevent cracking. After the retorts are all charged, the heat is raised to a temperature approaching whiteness. The odour of sulphurous acid may then be detected in the incondensable gases, especially if the charred mixture has not been sufficiently dried. Sulphides are next discoverable, and lastly, in about two or three hours, phosphorus. The distillation should be completed in about 16 hours, and after withdrawing the residues from the retorts and slightly cooling the furnace, the charging can be recommenced as before. Retorts, if carefully attended to, may last a considerable number of distillations.

When the temperature is fully up and phosphorus is coming off vigorously, the retorts should be examined by the spyholes, when the smallest flaw can be easily detected by the bright dazzling phosphorus flame which issues from the smallest crevice. When this is observable the retort should have its charge withdrawn, and the retort itself is then taken out and replaced by one from the kiln heated to the temperature of the phosphorus furnace, as has been already described. There is no difficulty in doing this, as the ports are intended to permit this very operation.

The chemistry of the process of preparing phosphorus from phosphoric acid may be described as follows:—The ortho-phosphoric acid liquor (H_3PO_4), after being mixed with carbon and heated to a dull red heat, is resolved into metaphosphoric acid (HPO_3), and when this is further heated to a high temperature in the retorts it is broken up by the carbon originally added and phosphorus distils over. The change may be thus represented:

$$4HPO_3 + 12C = 2H_2 + 12CO + P_4.$$

An example of the yield, &c., from a known amount of phosphoric acid may be of interest.

Quantities taken:—

502 lbs. of phosphoric acid liquor containing 25·7 p.c. free P_2O_5.

137 lbs. of coarse wood charcoal.

These were mixed together and dried in the manner described.

The dried mixture weighed 380 lbs.

On distillation the following results were obtained:—

Residue in retorts weighed 67 lbs.

Yield of *refined* yellow phosphorus, 38 lbs.

Theoretical yield, 56·2 lbs.[1] (Yield = 67·5 p.c.)

(*i*) *The Crude Phosphorus.* The phosphorus obtained in the condensers varies very much in appearance from a pale buff to a brick-red chocolate, or nearly black, colour. The colour is no doubt due to impurities, as well as to the presence of lower oxides of phosphorus and amorphous phosphorus. If condensed in *cold* water, it resembles the raspings of cork and floats on water. The crude product is ladled out of the condensing trough into malleable iron boxes provided with handles, in which it is carried to the refinery. Phosphorus in this condition is much more inflammable than it is in a pure state, and great care must be observed in the handling of it.

(*j*) *The Refining.* There is always more or less sand and clay mingled with the crude phosphorus, partly due to the unavoidable dust in the furnace-house and also to the luting. To get rid of this, it is advisable to fuse the crude product under hot water, and, after a thorough stirring with a wooden rake, to allow the mass to solidify, when it can be easily broken up with chisels, and is then of a uniform character.

The sand, clay, &c., mixed very frequently with some phosphorus, are left on the upper surface in a loose pulverulent condition. If these impurities are found to contain phosphorus, they may be distilled in an iron retort and the phosphorus recovered.

The solidified phosphorus is now ready for refining. The method described in text-books is to squeeze the melted phosphorus through chamois leather. A more rapid method is either to distil it in an iron retort or to refine by the use of chromic acid. The last method is probably the one most to be recommended. To carry out the refining by this process the crude phosphorus is first fused under water in a small lead-lined agitating pan provided with a lead steam-coil, and from 3–4 p.c. of bichromate of potash or soda (previously dissolved in water) is added. Sulphuric acid in equivalent proportion is next run into the agitator, and the whole is left to mix for 2 hours or more. After that time the phosphorus should be of a pale-yellow colour and almost transparent. The chrome liquors are now carefully syphoned off, and the phosphorus then receives a washing with hot water, after which it is syphoned off and rapidly filtered through a canvas filter-bag to remove the mechanical impurities. The phosphorus is now ready for moulding.

(*k*) *The Moulding.* The phosphorus melted under hot water may now be cast into 'wedges,' or made into 'sticks.' The 'wedges' or 'pains' (of the French manufacturer) are easily made. The liquid phosphorus is ladled under hot water into tin moulds $10\frac{1}{2}$ inches diameter by $4\frac{1}{2}$ inches deep, standing in a row in a shallow trough, and while still liquid a star-shaped arrangement, made also of tin, is dropped into the mould. The object of this is to divide the circle equally into 10 sectors or wedges. On solidifying the phosphorus by running in cold water into the trough and then removing it from the mould, 10 separate wedges are obtained in a convenient form for packing, each wedge weighing about 2 lbs. To admit of easy removal of the phosphorus, the tin mould divides into 2 parts and is made tight by india-rubber joints and flanges, &c.

If the phosphorus is desired in the form of 'sticks,' the fused element is drawn through glass tubes in an apparatus illustrated by the following sketches (Figs. 5 and 6):

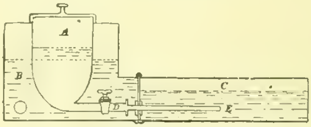

FIG. 5.—SECTION OF APPARATUS FOR MOULDING PHOSPHORUS INTO STICKS.

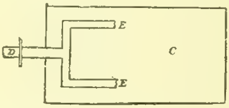

FIG. 6.—PLAN OF COLD WATER TANK FOR MOULDING PHOSPHORUS INTO STICKS.

A. Pot for melting phosphorus under water. B. Hot water tank heated with steam coil. C. Cold water tank, flanged to B. D. Cock for escape of liquid phosphorus. E. Metal tubes. (Same letters apply to figs. 5 and 6.)

Another method of moulding is to run the liquid phosphorus into slightly-tapered tin tubes made of a length to suit the tin packing-cases. The tubes are closed at one end by corks, and are set (corked end down) in troughs containing hot water, when the tubes are filled with the molten phosphorus. Cold water is run into the trough to solidify the latter, which is then removed from the moulds.

(*l*) *The packing.* The 'wedges' are packed along with water in tin cylinders, holding 50 kilos. of phosphorus. The dimensions of the cylinders are 22 inches deep by 11 inches diameter. The lids (11 inches diameter) are loose but fit tightly inside, and have a ¾ inch hole, through which water is poured after the lids are soldered on. These small holes are finally soldered up, and the cylinder is thus hermetically sealed and completely filled with water. Another size of case sometimes employed holds 25 kilos.; it is 12 inches deep by 11 inches diameter.

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[1] From phosphorus in free P_2O_5.

The tin packing cylinders should be provided with three wire handles—two opposite one another—at the upper part, and the third lower down near the base. These are found convenient in handling.

The sealed tins are now packed along with sawdust in rectangular wooden boxes 24 inches long by 12¼ inches broad × 12¼ inches deep. The wood is pine ⅝ inches thick. The boxes should be strengthened with hoop-iron at the edges. The sawdust is tightly rammed down between the tin case and the side of the box, and thus makes a firm and safe package.

When exporting phosphorus to certain countries—*e.g.*, Germany—the wooden boxes require to be further packed in canvas, and iron handles must be tightly fixed to either end of the box for convenience in lifting.

The 'stick' phosphorus is packed along with water in tins which hold 10 lbs. each. The tins are 7⅝ inches long by 5⅝ inches diameter; each one holds about 90 sticks (7½ inches long by ½ inch diameter).

The lids, &c., are soldered on as before described. These tins are further packed as in the case of 'wedges,' in wooden boxes holding ten in a box.

(*a*) *Other proposed methods of manufacture.* (1) Donovan proposed to mix phosphate of lead (obtained by acting on bones with nitric acid and then precipitating by acetate of lead) with finely-divided charcoal, and to distil for phosphorus.

(2) Fleck proposed to combine the manufacture of phosphorus with that of glue and gelatine. By this method the bones, freed from fat, are decomposed with weak hydrochloric acid, which dissolves out the phosphate of lime, leaving the cartilaginous matter insoluble. The acid phosphate liquor is evaporated, mixed with carbon, and distilled in suitable retorts.

(3) E. C. Mantrand (Eng. Pat. No. 1,166, May 25, 1854) patented a method of preparing phosphorus by decomposing an intimate mixture of phosphate of lime, carbonaceous matter, and silicious matter at a bright red or white heat in an atmosphere of hydrochloric acid or chlorine gas, when phosphorus, phosphuretted hydrogen, carbonic acid, &c., distil over.

(4) Wöhler suggested the method of decomposing phosphate of lime with silica and carbon, and distilling.

(5)[1] Gentele, in 1857, published a plan of phosphorus re-manufacture combined with the preparation of salammoniac. He treats the bones with hydrochloric acid. To the resulting solution crude carbonate of ammonia is added. The precipitated phosphate of lime so obtained is employed in the preparation of phosphorus, while the solution of chloride of ammonium is evaporated and sublimed for salammoniac.

(6)[1] Gerland (in 1864) suggests the treatment of bones with an aqueous solution of sulphurous acid.

(7)[1] Minary and Soudray (1865) proposed to prepare phosphorus from a mixture of phosphate of iron and well-ignited coke.

Besides the above, letters patent have been taken for the following methods of preparing phosphorus:

R. Lammy (Eng. Pat. No. 311 in 1857) grinds phosphate of ammonia with carbon, dries, and distils, producing ammonia first and then phosphorus.

R. A. Brooman (Eng. Pat. No. 2,294, 1864). Silica, iron, and coal are added to phosphate of lime in such proportion that silica can form with lime a fusible slag, and phosphide of iron is obtained. This latter may then be heated to quick redness with sulphur, sulphuretted hydrogen, bisulphide of carbon, &c., &c., to obtain phosphorus.

J. H. Player (Eng. Pat. No. 660 in 1866, and No. 1,064 in 1867) mixes phosphoric acid liquor evaporated to a thick paste with (1) spent tan or (2) with coal or coke in fine powder. He then carbonises to remove volatile matters, and distils the residue in clay retorts in the usual way.

E. Aubertin and L. Boblique (Eng. Pat. No. 2,458 in 1867) (1) mixes fine ground phosphate of lime with twice its weight of silica and 25 p.c. of coke, and heats to orange-red or white heat, when phosphorus comes off *without fusion*. No apparatus is described.

Claude Brison (Eng. Pat. No. 3,515 in 1868) patents the employment of a blast-furnace and blowing engine in the manufacture of phosphorus, and also the admixture in the blast-furnace of the fuel with the materials for producing the phosphorus. 'The mixture employed by preference for producing the phosphorus consists of phosphate of lime, silica, and carbonate of soda; the whole thoroughly desiccated.'

E. Aubertin (Eng. Pat. No. 1,593 in 1870) secured a further patent for producing phosphorus from phosphate of lime, silica and carbon. 1*st process:* By calcination in a furnace or retort at a temperature from 2192° to 2404°F. 2*nd process:* By fusion. Apparatus in this case is by preference a 'Fluss-ofen' blast-furnace, and the temperature is 2192° to 2932°F.

J. H. Player (Eng. Pat. No. 3,501 in 1872) proposes to utilise the waste gases from the retorts by passing them through a solution of sulphate of copper, whereby phosphide of copper is obtained.

J. Townsend (Eng. Pat. No. 1,862 in 1872) distils Redonda phosphate either along with carbon and a flux of common salt or borax, or with a mixture of sulphates of potash and soda, and so obtains phosphorus.

J. P. Serve (Eng. Pat. No. 49 in 1879) employs a furnace—either a reverberating or blast-furnace—or retorts, and claims (1) 'the preparation, in the form of blocks or bricks, of intimate mixtures and in suitable proportions, of phosphates of lime, &c., &c., and of silica or other silicious body bound or held together by a carburetted body such as tar-pitch or coal.' (2) The extraction of the phosphorus from the blocks or bricks. (3) A special construction of blast-furnace and condensers.

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[1] Wagner's Chemical Technology, p. 544.

[1] Wagner's Chemical Technology, p. 544.

A. Nicolle (Eng. Pat. No. 1,693 in 1888) decomposes mineral phosphate with nitric acid, and treats the resulting solution with sulphate of potash. He then filters from the sulphate of lime which is precipitated, and treats the filtrate with mercurous nitrate, thus obtaining phosphate of mercury. This is washed, dried, and distilled with carbon, when mercury is first obtained, and then phosphorus.

J. B. Readman (Eng. Pat. No. 14,962, in 1888) claims the application of heat produced by passing an electric current through the materials containing phosphorus placed in a closed furnace.

Parker and Robinson (Eng. Pat. No. 17,719, in 1888) claim the employment of electricity on similar lines to foregoing patent.

Folie-Desjardins (Eng. Pat. No. 13,240, in 1890) for a process for the simultaneous manufacture of phosphorus and of alkaline silicate—(1) by heating a mixture of the phosphate with one or more alkaline sulphates or carbonates with or without the addition of silicic acid or a flux in a reverberatory furnace, or in retorts within a regenerative gas-furnace, lixiviating the resulting mass, and evaporating solution to obtain the alkaline phosphates; (2) heating a mixture of the alkaline phosphate so obtained with silica and carbon in retorts placed in a regenerative furnace, thereby effecting the simultaneous production of phosphorus and an alkaline silicate.

Coignet (Eng. Pat. No. 2,970, in 1891) claims improvements in the moulding of phosphorus to avoid the carriage of much water in the packing cases.

The author has conducted during the last few years a large series of experiments (*v.* details in S. C. I., vols. 9, 10) with the view of obtaining phosphorus by distillation, *direct* from the raw phosphate of lime, without the employment of sulphuric acid at all or the preparation—as an intermediate stage—of phosphoric acid. He has proved conclusively that silica in the form of sand, ganister, or flints intimately mixed with phosphate of lime and carbon, in suitable proportions, is capable, at a high temperature, of effecting the decomposition of the phosphate, expelling practically all the phosphorus contained in the mixture, leaving, as a residue, a fluid slag. Further, that with adequate condensing appliances a very large proportion of the phosphorus so expelled may be collected. Similarly, satisfactory results have been obtained by the employment of other phosphates, such as phosphate of alumina, &c., provided fluxes suitable for each case are employed.

Retorts were found unsuitable for the distillation, both on the score of economy and durability, and the blast furnace, which was tried for some time, presented many practical difficulties in its working.

The success of the application of electricity to the production of certain metals and alloys, notably those of aluminium, led him to try that source of energy for the production of phosphorus, and the result has been that the author, along with T. Parker (who applied for letters patent only a few weeks after the author's application) (Readman's patent, No. 14,962, 18th Oct. 1888; Parker and Robinson's patent, No. 17,719, 5th Dec. 1888; A System of Inorganic Chemistry, by W. Ramsay, p. 666) arranged for the erection of a large experimental plant with engines, dynamos, and electric furnaces capable of turning out about 40 cwt. of phosphorus per week.

The object which has now been successfully attained in the new process, called the Readman-Parker and Robinson system, is the *continuous* production of phosphorus *direct* from raw materials by means of the electric furnace, the heat being applied in and through the phosphorus-bearing mixture in the furnace, and not, as in the case of distillation, in retorts, heated from the outside, involving, in consequence, a great expenditure of fuel.

The process is carried out as follows. The phosphate, carbon, and fluxes, in proper proportions and all carefully and intimately mixed together, are introduced (previously heated to as high a temperature as possible) into the upper part of the electric furnace by means of a tight-fitting hopper arrangement, the electric current is led to and from the furnace by copper cables connected to large carbon electrodes situated on either side of the furnace. The furnace itself is practically an iron tank, lined inside with refractory bricks, thus making a kind of brick-sided trough about 18 inches square and 36 inches deep, closed at the top by the hopper referred to, and having an outlet pipe to the condenser placed on the upper part of the side of the furnace.

After the charging of the furnace, the current is turned on, and soon indications of phosphorus may be seen in the condensers. The gases escaping by the side pipe pass on to a series of copper condensers, the first of which contains hot and the others cold water, when they are allowed to escape into the air. As the phosphorus is distilled off from the mixture the residue in the furnace forms a liquid slag, which from time to time is tapped out at the bottom of the furnace, fresh phosphorus-bearing mixture being introduced by the hopper at the top precisely as in blast-furnace practice, where closed tops are used. In this way the operation is made continuous, and is carried on for days without cessation.

The mixed materials, as introduced into the electric furnace, can be had to contain about 14 p.c. of elementary phosphorus, and as the weight of the slags from these is not so much as half the weight of the original mixture, and as, moreover, the slag on an average contains only about 1 p.c. of phosphorus, it will be apparent that the decomposition is remarkably complete.

The crude phosphorus obtained in the condensers is refined in the way previously described.

The advantages of this process may be summarised as follows. No sulphuric acid is required, no need to prepare and concentrate phosphoric acid, much less handling of materials, no fire-clay retorts employed, less loss during process, larger yields, and less consumption of coal.

The Production of Amorphous Phosphorus.

Amorphous phosphorus in compact pieces is a reddish brown, moderately hard substance,[1] somewhat resembling in appearance the hematite iron ore of Cumberland. It is opaque, with a slight metallic lustre. It is brittle and easily broken, and exhibits a conchoidal iron-black fracture with sharp edges.

The sp.gr. of amorphous phosphorus is 2·25. It is without taste or smell, is unattacked by most solvents, and if taken internally is excreted unchanged.

Amorphous phosphorus, as met with in commerce, frequently contains small quantities of ordinary phosphorus, from about ½ p.c. downwards according to Fresenius; in addition, it usually contains phosphoric acid, graphite, and other impurities, and has generally an acid reaction.

The following is an analysis of amorphous phosphorus:—

	Per cent. (Readman)
Phosphorus	93·44
Phosphoric acid . . .	3·58
Oxide of iron and alumina .	·78
Alkalis, carbon, loss, &c. .	·84
Insoluble in nitric acid. .	1·36
	100·00

Ground amorphous phosphorus dissolves very easily in nitric acid on account of its state of sub-division.

Chlorine has no action on this variety of phosphorus unless the latter is heated, when it burns with a yellow flame.

For ignition, amorphous phosphorus requires a temperature of at least 240°C.

(*a*) *The apparatus and process.* The conversion of yellow into amorphous phosphorus is effected by heating the former to a temperature between 240° and 250°C. for some time.

The apparatus employed is a cast-iron pot which is closed with a cover. A narrow tube open at both ends is screwed into the upper part of the pot. This acts as a safety valve, and avoids all risk of explosion.[2]

If pressure be employed within the pot and the temperature exceeds 300°C., the yellow is transformed into amorphous phosphorus in a very short time. There is, however, considerable danger in this treatment which might far outweigh the economy in time. According to the method used, when the conversion is effected in open iron vessels in which the air finds but limited access, the process, though tedious, is free from all difficulty or danger.

Ordinary phosphorus may also be converted into amorphous phosphorus by chemical action, as by heating it to 200°C. with a small quantity of iodine (Brodie, C. J. 5, 289).

(*b*) *The refining.* The amorphous phosphorus, obtained in the cast-iron pots, is in hard compact lumps. These are ground under water, and freed from ordinary phosphorus by boiling the ground powder with a solution of caustic soda; it is then repeatedly washed with boiling water and carefully dried by steam heat.

(*c*) *The packing.* The ground red phosphorus, dried in the manner described, is sent out in the dry state in tin boxes holding 10 lbs. each.

Properties of Ordinary Phosphorus.

Phosphorus at the ordinary temperature (15°C.) is a pale yellow, soft and flexible, translucent, waxy-looking solid, which becomes hard and brittle at temperature below 5·5°C. It is extremely inflammable, especially if not quite pure, and must always be kept under water. It has a great affinity for the oxygen of the air, with which it combines directly.

It also combines *directly* with chlorine, bromine, iodine, and sulphur, but not with nitrogen and hydrogen.

Phosphorus is luminous in the dark, and in a moist atmosphere a gradual oxidation takes place with formation, first of phosphorous acid, and ultimately of phosphoric acid, ozone and hydrogen dioxide being likewise produced at the same time. When exposed to daylight, under water, a whitish incrustation is formed, which frequently becomes of a reddish hue. According to Baudrimont (C. R. 61, 857, 1866) the crust is formed only under influence of oxygen, and possesses all the usual properties of ordinary phosphorus.

The following determinations were recently made by the author, with the help of his assistant (G. H. Gemmell):—

Specific gravity at 16°C., 1·82.

Melting-point, under water in an open vessel, 43·3°C., and in closed vessel without water phosphorus melts at 30°C. In both cases, if left undisturbed in a smooth glass vessel it may remain liquid at temperatures considerably below the melting-points. It distils at 269°C., the vapour being colourless, and takes fire in air when heated to 34°C. It is very soluble in bisulphide of carbon, one part dissolving 9·26 parts of phosphorus, a slight amount of heat being developed, but on cooling to ordinary temperatures some of the phosphorus is precipitated in a crystalline form.

Phosphorus is also very soluble in sulphur chloride, phosphorus trichloride, and phosphorus sulphide. It is nearly insoluble in water.

The following table shows the weight of different solvents required to dissolve 1 part by weight of phosphorus. The temperature of the solvent, unless otherwise stated, is 12°C.:—

	Parts
Benzene (90 p.c. sp.gr. ·878) .	82·5
Chloroform	83
Aniline	154
Oil of turpentine . . .	162
Paraffin oil (sp.gr. ·806) . .	179
Ethyl ether (sp.gr. ·725) . .	203
Olive oil	[illegible]
Alcohol (sp.gr. ·801) . . .	764
,, ,, ,, at 40° .	535
Wood spirit (sp.gr. ·846) . .	1408
,, ,, ,, ,, at 40° .	862
Acetone	2702
Solution of caustic soda (sp.gr. 1·35)	194
Liquor ammoniæ (sp.gr. ·880) .	3030

The ammoniacal solution becomes dark brown, and the surface of the phosphorus is coated with a brown-black deposit. When water is added to the greater number of the above solutions, the phosphorus is precipitated.

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[1] The hardness of amorphous phosphorus lies between calc. [illegible]

[2] See English Patent No. [illegible], by A. [illegible]

Cold concentrated nitric acid dissolves phosphorus. If exposed to the action of dilute nitric acid for some time its crystalline character becomes evident.

Sulphuric acid (92 p.c. O.V.) does not dissolve phosphorus in the cold, but attacks it on prolonged boiling. Phosphorus is insoluble in cold concentrated hydrochloric acid.

Phosphorus fumes in the air, emitting a garlic-like odour. On exposure to air, it not unfrequently melts and takes fire, and during combustion dense white fumes of P_2O_5 are produced, which can be collected in snowy flakes. The burns produced by ignited phosphorus are of a serious nature, and are very slow in healing, any unconsumed phosphorus left on the wound being most difficult and painful to remove.

Phosphorus sometimes contains a small proportion of arsenic derived from the sulphuric acid used in the preparation of the phosphoric acid. If this be present in any quantity the refined phosphorus has a red or mahogany colour. Phosphorus is a powerful poison; less than 2 grains are said to have caused death. Those who have to handle it frequently are liable to necrosis, which begins with the disintegration of the jaw-bones, and ends with their total destruction. Ill-fed and scrofulous persons are said to be specially affected. It is rather a curious circumstance that persons engaged in the manufacture of phosphorus do not appear to be affected by this disease.

Phosphorus does not conduct electricity (Faraday).

According to Deville and Troost, the vapour of phosphorus has a sp.gr. of 4·50 at 1040°C.; it is concluded, therefore, that there are four atoms in the molecule.

Phosphorus is tough, and cannot be pulverised; but if melted under water and shaken till the fluid is quite cold, it is reduced to a fine state of division in the form of round pellets of various sizes; an aqueous solution of urea or alcohol aids this formation. When heated with aqueous vapour to a temperature of 250°C., phosphorus decomposes the water, phosphorous acid and phosphuretted hydrogen being formed.

Phosphorus volatilises to a small extent when boiled with water.

Phosphorus *in vacuo* volatilises at ordinary temperatures. It is not luminous in pure oxygen at temperatures below 20° (Müller); but if mixed with a neutral gas, or if it be rarefied, then luminosity is at once seen (Graham). The presence of mercuric chloride and of phenol (Polstroff and Mensching, C. N. 57, 71), and of certain gases, such as olefiant gas, sulphuretted hydrogen, or the vapours of turpentine or ether when present even in small quantities, prevent the glow of phosphorus. When phosphorus is placed in an atmosphere of hydrogen, nitrogen, or carbonic acid, these gases when brought into contact with oxygen become luminous from the oxidation of the phosphorus diffused through them.

Phosphorus at high temperatures combines with most of the metals forming phosphides. For example, if phosphate of lime and silica with carbon and iron (as ore or metal) be heated to a high temperature, a very fusible phosphide[1] of iron can be obtained, corresponding to the formula Fe_2P.

Phosphorus, owing to its affinity for oxygen, is a powerful reducing agent. It precipitates copper, silver, platinum, palladium, and gold when brought into a solution of the salts of these metals.

Besides the red or amorphous, there appears to be a third allotropic modification of phosphorus—viz., metallic or rhombohedral phosphorus—formed by heating the element in sealed tubes along with metallic lead for some hours. On cooling, crystals are found permeating the lead; these are separated by dilute nitric acid, which dissolves out the lead. This phosphorus is a dark crystalline substance, sp.gr. 2·34 at 15·5°.

H. M. Vernon (Phil. Mag., October 1891) states that a rhombic modification of phosphorus exists, melting at about 45·3°, and of sp.gr. 1·8272. It appears to be formed from the octahedral variety by slowly cooling it when liquid.

Uses of phosphorus and statistics of the trade. The chief consumption of phosphorus at present is in the manufacture of matches. This is by far the largest and most important use for the element. The so-called 'Safety matches' which ignite on the box, have no phosphorus on the match itself, but have a thin layer of red or amorphous phosphorus on the sides of the box.

Phosphorus is used in medicine in small doses. It is likewise employed in form of a paste for the destruction of rats and mice, and recently a considerable quantity has been exported to the Australian Colonies to assist in the extermination of the rabbit. Phosphorus is also required in the manufacture of saccharin.[2] It is also used in the laboratory, and in the manufacture of many organic compounds.

Phosphorus as phosphide of calcium is one of the constituents of the material used for distress signalling at sea.

Sir William Armstrong's explosive mixture for shells is said to contain amorphous phosphorus and chlorate of potash.

Phosphor bronze, which is now extensively employed in the arts, contains a small percentage of phosphorus, which modifies the properties of copper to a large extent favourably when present in minute quantities, and unfavourably if present in more than 2 to 3 p.c.

At the present time nearly the entire amount of phosphorus manufactured in Europe is supplied by two establishments—viz., Messrs. Albright and Wilson, of Oldbury, Birmingham, and Messieurs Coignet et fils, of Lyons. There are one or more makers of phosphorus in Russia, but the production in that country is believed to be small.

It is difficult to ascertain with any degree of accuracy the exact amount of phosphorus consumed every year. The large total of 1,200 tons has been mentioned as an approximation to the truth, although probably this figure is rather below than above the quantity.

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[1] Further experiments detailed in Percy's Metallurgy, 'Iron and Steel,' p. 70.

[2] See British Association Report, Manchester, 1887.

The following details of the total amount of hosphorus per box of matches, made by a few of the well-known match manufacturers, may be of interest:—

Description of match	Manufacturer	No. of matches per box	Total phosphorus in grms.	Phosphorus used
Wax vestas, in box 6½ inches long	Bell & Co.	360	6·33 on matches	Ordinary
Wax vestas, in box 3 inches long, red tips	"	150	2·22 "	"
Wax vestas, 'Star,' in box 6½ inches long	Mariotte & Co.	350	6·89 "	"
Safety matches (wood), in box 3 inches long	Bell & Co.	82	1·07 on box	Amorphous
Safety matches (wood), in box 3 inches long	Bryant & May	72	·58 "	"
Steamer safety match (wood)	Not stated	100	·49 "	"
Jubilee matches (wood)	Bell & Co.	84	1·76 on matches	Ordinary
Vulcan paraffin match (wood)	Made in Sweden	96	1·04 "	"
Vesuvians (wood) (double-headed)	Bryant & May	21	1·74 "	"
Flaming vestas (wax)	Bell & Co.	36	·51 "	"

J. B. R.

PHOSPHORUS, NON-METALLIC COMOUNDS OF.

Hydrogen phosphides. Three of these comounds, PH_3, P_2H_4, and P_4H_2(?) are known, the st being gaseous, the second liquid, at ordinary mperatures, and the last solid. According to ommaille (C. R. 68, 263), a second solid phosnide, P_3H, is obtained by the action of ammonia lution on phosphorus.

P [illegible] n, or *phosphine*, PH_3, is usually obtained by eating phosphorus with milk of lime or strong otash: $3KHO + 3H_2O + P_4 = PH_3 + 3POH_2KO$, by decomposing calcium phosphide with ater: $3Ca_2P_2 + 12H_2O = 4PH_3 + P_2 + 6Ca(HO)_2$.

As thus prepared, the gas contains a suffient amount of the dihydride, P_2H_4, probably oduced by a secondary reaction,

$$Ca_2P_2 + 4H_2O = 2Ca(HO)_2 + P_2H_4,$$

render it spontaneously inflammable. When e gas is passed through water, each bubble on tering the air gives rise to a vortex ring of osphoric oxide or metaphosphoric acid. The s also contains hydrogen produced by the adual decomposition of the hypophosphite by e alkali: $POH_2KO + 2KHO = 2H_2 + K_3PO_4$.

The spontaneous inflammability may be deoyed by decomposing or condensing the dihyde by exposure to light, or by passage through ube cooled by a freezing mixture.

The trihydride may be obtained free from the ydride by decomposing calcium phosphide h hydrochloric acid, which converts any ydride formed into the gaseous and solid drides. It may be prepared pure by decomsing phosphonium iodide with water, or preably with potash,

$$PH_4I + KHO = PH_3 + KI + H_2O$$

ofmann, B. 4, 200).

Phosphine is a colourless gas with an offen- garlic-like smell, somewhat soluble in ter, and combining, like ammonia, with cer- metallic chlorides, and with hydrobromic and hydriodic acids to form phosphonium compounds.

Gattermann and Hausknecht (B. 1890, 1174) employ the following process for preparing the dihydride. A large three-necked Woulff's bottle, three-fourths filled with water, is freed from air by a current of hydrogen supplied through a tube fitted in one neck and dipping just beneath the water, and is heated in a water-bath to 60°. Calcium phosphide is then introduced in lumps weighing about two grms. through a wide, funnel-topped tube fitted to the second neck and just dipping beneath the water. The evolved gases pass through a tube fitted to the third neck to a test-tube, from which passes a tube to a condensing-tube surrounded by iced water. The water in the gas condenses in the test-tube, and the hydride, P_2H_4, liquefies in the condenser, about 2 c.c. being obtained from 50 grms. of calcium phosphide. The uncondensed gas may be passed through a flask containing hydrochloric acid, which decomposes the remaining P_2H_4 into the trihydride and the solid hydride.

The dihydride is a colourless liquid of sp.gr. 1·007 at 12°, boiling, when not too suddenly heated, at 57-58° (735 mm.) (Gattermann and Hausknecht, *l.c.*). On exposure to light, or under the action of hydrochloric acid, it decomposes into the trihydride and the solid hydride. Small quantities of the dihydride impart spontaneous inflammability to hydrogen, carbon monoxide, and other combustible gases.

The solid hydride is obtained, as above, as a yellow powder, by decomposing the dihydride with hydrochloric acid, or by the action of light, or by treating calcium phosphide with hot hydrochloric acid. It ignites when heated in the air.

[illegible] *nitrogen.*

A considerable number of these compounds exists.

[illegible] is obtained as an amorphous, yellowish-white powder, insoluble in water and infusible at a red-heat, when phosphorus trichloride, cooled by a freezing mixture, is saturated with ammonia gas, and the product ($5NH_3.PCl_3$?) is heated in a current of carbon dioxide so long as ammonium chloride passes off.

Phosphamide (*phosphodiamide*) $PONHNH_2$ is a white powder obtained by the action of water on the product of the action of ammonia on phosphorus pentachloride:

$$PCl_5 + 4NH_3 = (NH_2)_2PCl_3 + 2NH_4Cl$$

and

$$(NH_2)_2PCl_3 + H_2O = PONHNH_2 + 3HCl.$$

Phosphoryl triamide (*phosphotriamide*) $PO(NH_2)_3$ is a white amorphous powder obtained by the action of dry ammonia on phosphorus oxychloride (Schiff, Z. 5, 609).

Phosphoryl nitride (*phosphomonamide*) PON is obtained when either of the last two compounds is heated to redness out of contact with the air. Several phosphamic acids, and amides containing chlorine, are also known (*v.* Gladstone, C. J. 1864, 225; 1865, 1; 1866, 1 and 290; and Salzmann, B. 7, 494).

Compounds of phosphorus and sulphur.

Several liquid and solid sulphides, all of which are very inflammable and more fusible than either of the constituent elements, are known. The liquid compounds SP_4 and SP_2 may be prepared by combining the two elements in proper proportions by warming under water. The solid sulphides P_4S_3, P_2S_3, and P_2S_5 are obtained by carefully heating sulphur with amorphous phosphorus. The composition P_2S_6 (Dupré) or P_2S_{12} (Berzelius, Gmelin's Handb. 2, 218) has been assigned to a body obtained in rhombic sulphur-like crystals by solution of sulphur in sulphur diphosphide. According to Ramme (B. 12, 940 and 1350), the crystals are merely sulphur containing phosphorus.

Phosphorus pentasulphide P_2S_5, which is employed in the preparation of organic sulphur compounds is produced by gently heating a mixture of powdered roll sulphur and amorphous phosphorus in a loosely-corked flask, best in a stream of carbon dioxide. The product forms a greyish-yellow crystalline mass, which may be obtained in transparent crystals by sublimation. It melts at 274–276° (Meyer, B. 12, 610), and boils at 519° at 734 mm. pressure (Goldschmidt, B. 15, 304). For recent work on phosphorus sulphides, *v.* Rebs (A. 246, 356), Dervin (Bl. 41, 433), Isambert (C. R. 96, 1499 and 1771), Lemoine (C. R. 96, 1630), and Schulze (B. 16, 2066).

Compounds of phosphorus and selenium.

The selenides P_4Se, P_2Se, P_2Se_3, and P_2Se_5, corresponding with the sulphides of phosphorus, are produced by gently heating a mixture of dry phosphorus and selenium in a stream of hydrogen (*v.* Berzelius, Gmelin's Handb. 2, 242; Bogen, A. 124, 57; and Hahn, J. pr. 93, 430).

Haloid compounds of phosphorus.

Phosphorus trichloride PCl_3, may be prepared by passing dry chlorine over heated amorphous phosphorus or over dry ordinary phosphorus, and digesting the product with ordinary phosphorus for some weeks to convert any pentachloride which may have been formed into the trichloride (Dumas, A. Ch. [3] 55, 172). It is a mobile, colourless, fuming liquid of pungent smell, boiling at 75·95° (760 mm.), and having a sp.gr. of 1·61275 $\frac{0^\circ}{4^\circ}$ (Thorpe, Pr. 24, 295). It absorbs water with production of hydrochloric and phosphorous acids. It dissolves phosphorus, and is itself soluble in benzene and carbon bisulphide. When mixed with alcohol, heat is evolved, with production of ethyl chloride and phosphorous acid, and evolution of hydrochloric acid. Phosphorous ether is also produced (Béchamp, C. R. 40, 944; and 41, 23).

Phosphorus pentachloride PCl_5 may be obtained by passing dry chlorine over the well-cooled trichloride until the whole is dry, or by the action of excess of chlorine on phosphorus. On the large scale, it is best prepared by passing excess of dry chlorine through a cooled solution of phosphorus in carbon bisulphide, and finally crystallising out the product. It forms white lustrous crystals of unpleasant smell, volatilising below 100° without liquefying. Under pressure, it melts at 148° (Strecker). The vapour decomposes, when heated, into the trichloride and chlorine (Wanklyn and Robinson, Pr. 12, 507).

In moist air, the pentachloride is converted into the oxychloride with evolution of hydrochloric acid. Sulphur trioxide converts it into the oxychloride with production of sulphuryl chloride: $SO_3 + PCl_5 = SO_2Cl_2 + POCl_3$. Phosphorus pentachloride is much used in the preparation of organic chlorides.

Phosphorus chlorobromide PCl_3Br_2 is obtained by the action of bromine on phosphorus trichloride. It solidifies at $-20°$, and decomposes when heated to 35° (Michaelis, B. 5, 9). It combines with various proportions of bromine (*v.* Michaelis, *l.c.*; Prinvault, C. R. 74, 868; and Stern, C. J. 1886, 815).

Phosphorus chloro-iodide PCl_3I is said to be obtained in fine red hexagonal crystals by the action of iodine on phosphorus trichloride (Moot, B. 13, 2029).

Phosphoryl chloride $POCl_3$ may be prepared by heating dry oxalic or boric acid with the pentachloride:

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO,$$

or by heating the pentachloride with the pentoxide in a sealed tube: $3PCl_5 + P_2O_5 = 5POCl_3$. Dervin (C. R. 97, 576) recommends its preparation by the action of potassium chlorate on phosphorus trichloride.

Phosphoryl chloride is a colourless, fuming liquid, boiling at 107·23° (760 mm.), and having a sp.gr. of 1·71163 $\frac{0^\circ}{4^\circ}$ (Thorpe, C. J. 37, 338). When cooled it solidifies to crystals which melt at $+0·8°$. Its molecular depression of the freezing-point is 0·48° (Huntley, C. J. 1891, 205). Water instantly decomposes it into hydrochloric and phosphoric acids.

Metaphosphoryl chloride (?) PO_2Cl. A straw-coloured viscous body obtained by heating a mixture of phosphorus pentoxide and phosphoryl chloride in a sealed tube at 200° (Gustavson, B. 4, 853), or together with phosphoryl chloride, by the action of chlorine on cooled phosphorous oxide (Thorpe and Tutton, C. J. 1890, 572); has been found to possess a composition corresponding with the formula PO_2Cl. It has, however, been shown by Huntley (C. J. 1891, 202) that this body consists of at least two substances, one of which is pyrophosphoryl chloride, while the other is a compound or mixture of the composition $P_7O_{13}Cl_5$.

Pyrophosphoryl chloride $P_2O_3Cl_4$ is a colourless, fuming liquid, boiling above 210°. It is obtained by the action of nitrogen peroxide on cooled phosphorus trichloride. Nitrosyl chloride is evolved, and pyrophosphoryl chloride remains together with phosphorus pentoxide, phosphorus trichloride, and phosphoryl chloride, from which it is separated by fractional distillation (Geuther and Michaelis, B. 4, 767). It is also obtained as stated above.

Phosphoryl bromochloride $POBrCl_2$ (*v.* Menschutkin, J. pr. 98, 485) is a highly refractive liquid, boiling at 137·6° (760 mm.), and having a sp.gr. of 2·12065 $\frac{0^\circ}{4^\circ}$ (Thorpe, C. J. 37, 344). When cooled, it solidifies in tables, which melt at 11° (Geuther and Michaelis, B. 4, 769).

Thiophosphoryl chloride $PSCl_3$, is a colourless, fuming liquid, produced by the action of sulphuretted hydrogen on the pentachloride, or, better, by heating a mixture of phosphorus pentasulphide and pentachloride. It boils at 125° (760 mm.), and has a sp.gr. of 1·6682 $\frac{0^\circ}{4^\circ}$ (Thorpe, C. J. 37, 341).

Nitrogen chlorophosphide $P_3N_3Cl_6$ is obtained by gently heating a mixture of phosphorus pentachloride and mercurammonium chloride (white precipitate) or ammonium chloride. It sublimes in rhombic prisms, melting at 110°, and boiling at 240° (*v.* Gladstone and Holmes, C. J. 17, 225).

Phosphorus tribromide PBr_3 is best prepared by slowly dropping bromine on excess of amorphous phosphorus in a flask fitted with an inverted condenser. The rectified product is a colourless mobile liquid of strong, pungent smell, boiling at 172·9° (760 mm.), and having a sp.gr. of 2·923 $\frac{0^\circ}{4^\circ}$ (Thorpe, C. J. 37, 335).

Phosphorus pentabromide PBr_5 is produced by the addition of bromine to the cooled tribromide, in the form of yellow crystals of pungent smell, melting to a red liquid, which decomposes into the tribromide and bromine at 100°.

Phosphoryl bromide, phosphorus oxybromide $POBr_3$ occurs in flat tables, melting at 45°–46° and boiling at 195° (Ritter, J. 8, 301), and is prepared similarly to phosphoryl chloride.

Phosphonium bromide PH_4Br crystallises in colourless cubes, and resembles the iodine compound.

Thiophosphoryl bromide $PSBr_3$, a yellow, crystalline body, *pyrothiophosphoryl bromide* $P_2S_3Br_4$, a fuming yellow oily liquid, and *metaphosphoryl bromide* PS_2Br, are also known.

Phosphorus di-iodide P_2I_4 is prepared by the gradual addition of 8·2 parts of iodine to a solution of 1 part of phosphorus in carbon bisulphide. On distilling off the bisulphide, or on cooling it, the iodide remains or crystallises out in bright orange-yellow crystals which fuse at about 110° (Corenwinder, A. Ch. [3] 30, 242).

Phosphorus tri-iodide PI_3 is prepared similarly to the di-iodide, but with the use of a correspondingly larger proportion of iodine. It forms red six-sided deliquescent prisms, using at 55° (Corenwinder, *l.c.*).

According to Burton (Am. 3, 280), *oxyiodides* of the formulæ $I_6P_4O_5$ and I_2PO_2 exist.

Phosphonium iodide PH_4I is obtained by the union of phosphine with hydriodic acid, or by the action of water and iodine on excess of phosphorus.

The iodine and phosphorus are preferably combined in carbon bisulphide, which is then distilled off and the water added gradually during passage of carbon dioxide (Hofmann, B. 6, 291). The iodide is thus obtained as a sublimate of glittering deliquescent quadratic prisms, decomposed by water into hydriodic acid and phosphine. It is a powerful reducing agent, and is employed as such in the preparation of many organic compounds.

Phosphorus trifluoride PF_3 may be prepared by carefully heating dry copper phosphide with lead fluoride, or by allowing arsenic tri-fluoride to drop upon phosphorus tri-chloride, or, preferably, by gently warming a mixture of dry zinc fluoride and phosphorus tribromide. It is a colourless sharp-smelling gas, which condenses at −10° under a pressure of 40 atmospheres to a colourless mobile liquid without action on gas. The gas dissolves slowly in water. It produces silicon fluoride, with separation of phosphorus when heated in contact with glass. It combines directly with bromine, giving an amber-coloured mobile liquid having the composition PF_3Br_2 (Moissan, C. R. 99, 655, and 970, 100, 272 and 1,348; A. Ch. [6] 19, 286).

Phosphorus pentafluoride PF_5 is obtained by the action of arsenic trifluoride on phosphorus pentachloride (Thorpe, Pr. 1876, 122). It is a very heavy, fuming, colourless, uninflammable gas, which is rapidly decomposed by water into hydrofluoric acid and phosphoric acid, and which may be liquefied under pressure. It combines with dry ammonia to produce a white solid $2PF_5.5NH_3$, and, according to Tassel (C. R. 110, 1,261), combines with nitrogen peroxide to produce a white crystalline body of the composition $PF_5.NO_2$; *v.* also Moissan (C. R. 101, 1,490 and 103, 1,257).

Phosphoryl fluoride, phosphorus oxyfluoride POF_3 may be prepared by the action of the electric spark on a mixture of phosphorus trifluoride and oxygen, by the action of phosphorus oxychloride on gently warmed zinc fluoride (Moissan, C. R. 102, 1,245), or, better, by the method employed by Thorpe and Hambly (C. J. 1889, 759), which consists in gently heating a mixture of cryolite and phosphorus pentoxide. It is a colourless, fuming gas, rapidly absorbed by water, and without action when dry on glass or mercury.

Thiophosphoryl fluoride PSF_3 may be obtained by heating a mixture of arsenic trifluoride and phosphorus thiochloride in a sealed glass tube to 150°, or by heating a mixture of amorphous phosphorus, sulphur, and lead or bismuth fluoride, or, preferably, by heating a mixture of powdered, freshly-fused lead fluoride, and freshly-made phosphorus pentasulphide in a leaden tube from which air has been expelled by a current of dry nitrogen: $P_2S_5 + 3PbF_2 = 3PbS + 2PSF_3$. The action commences at 170°, and the temperature should be kept below 250°. The gas is stored over mercury in a glass holder containing fragments of quicklime, which gradually absorb the phosphorus trifluoride and any trace of silicon fluoride contained in the gas. The quicklime should be freed from air before use by repeatedly passing dry nitrogen into the holder and exhausting with a Sprengel pump. At ordinary temperatures, thiophosphoryl fluoride is a heavy colourless gas which condenses at a pressure of 10 to 11 atmospheres to a colourless liquid. A jet of the gas burns spontaneously with a greyish-green flame of extremely low heating power. If a considerable quantity of the gas be suddenly exposed to the air, a fine blue flash, followed by the greyish-green flame, is observed. The gas burns spontaneously with a yellow flame in oxygen, but the dry gas does not inflame in dry oxygen in presence of sufficient of its oxidation products. The mixture instantly inflames on exposure to air or on introduction of moisture.

When heated or exposed to the electric spark, the gas is decomposed into sulphur, phosphorus, and phosphorus fluorides. It is without action on mercury, sulphuric acid, carbon bisulphide, or benzene. It dissolves to some extent in ether, the solution burning with a greenish flame. It dissolves slowly with decomposition in water and solution of potash, soda, or ammonia. It combines with ammonia gas to form a white solid. Gently heated sodium burns with a red flame in the gas, the residue evolving spontaneously inflammable phosphine when treated with water. When heated in a glass tube the gas deposits phosphorus and sulphur, with formation of silicon tetrafluoride, which occupies three-fourths of the volume of the original gas: $4PSF_3 + 3Si = 3SiF_4 + P_4 + S_4$ (Thorpe and Rodger, C. J. 1888, 766, and 1889, 306).

Oxides and acids of phosphorus.

The product of the combustion of phosphorus in a limited supply of air consists of a mixture of the four oxides P_4O, P_4O_6, P_2O_4, and P_2O_5.

The first of these oxides, P_4O, has been shown by Le Verrier (A. 27, 167) to constitute the light red or orange constituent which was formerly supposed to be amorphous phosphorus.

Phosphorous oxide, phosphorous anhydride P_4O_6. The existence of this compound as one of the products of the slow combustion of phosphorus seems to have been first noticed by Sage in 1777. It appears also to have been obtained by Cabell as a sublimate from the mixed oxides (C. N. 50, 209). It, however, received no systematic examination until Thorpe and Tutton (C. J. 1890, 545) obtained it in a state of purity by the following method:—

Pieces of dried phosphorus are placed in a glass tube drawn out, but open at one end, and connected at the other end with a brass tube surrounded by a tube filled with water. The inner tube is fitted to a long-limbed U-tube formed at the bend, with a branch fitted to a small bottle, into which the product of the action may be passed by warming the limbs of the U-tube. A freezing mixture surrounds the U-tube and bottle.

The phosphorus having been ignited by heating the tube, is oxidised by drawing air through the apparatus with an aspirator, and after about fifteen minutes, the water around the brass tube is heated to about 50°, as indicated by a thermometer fitted to the outer tube, and the temperature is maintained thereabouts until near the end of the operation, when it is raised to about 60°. The readily fusible trioxide gradually passes over from the combustion products in the brass tube and solidifies in the U-tube, a loose plug of glass wool in the brass tube preventing passage of the other oxides. The action is stopped when about four-fifths of the phosphorus has been burned, in order to diminish the chance of oxidising the product.

The product solidifies in the U-tube as a snow-white waxy mass. It may also be obtained in long feathery aggregations or in thin isolated prisms, terminated by pyramids, and probably belonging to the monoclinic system, as do those of the corresponding compound with arsenic or antimony.

Phosphorus trioxide possesses a peculiar phosphorus-like smell. It fuses at 22·5° to a mobile liquid which normally re-solidifies at 21°, but which sometimes exhibits the property of superfusion. It boils at 173·1° (760 mm.). When heated in a sealed tube to about 210° the oxide becomes turbid, and at 440° is entirely decomposed into the tetroxide and amorphous phosphorus.

Phosphorous oxide is slowly dissolved by cold water, forming phosphorous acid. With hot water, the action is violent, large quantities of the red suboxide or amorphous phosphorus being produced, with evolution of spontaneously inflammable phosphine.

Phosphorous oxide dissolves unchanged in ether, carbon-bisulphide, benzene, and chloroform, but instantly ignites in contact with absolute alcohol. When this action is properly controlled, *di-ethyl phosphorous acid* is obtained.

The oxide is spontaneously oxidised in presence of air or oxygen. When thrown into oxygen heated at 50° or 60°, it ignites with great brilliancy. It inflames readily when exposed to the air, especially when warmed or when in contact with fabrics or paper. When thrown into chlorine, it burns with a greenish flame. The slow action of chlorine on the cooled oxide gas gives a mixture of phosphoryl chloride and the so-called metaphosphoryl chloride.

Bromine acts in a similar manner, but with previous formation of phosphorus pentabromide. With iodine it forms the tetraiodide and the pentoxide: $5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5$. Heated with sulphur it yields phosphorus sulphoxide $P_4O_6S_4$, forming clear transparent crystals, m.p. 120° and b.p. 295°, deliquescing rapidly in the air, and readily dissolved by water, forming sulphuretted hydrogen and phosphoric acid: $P_4O_6S_4 + 10H_2O = 4H_3PO_4 + 4H_2S$ (Thorpe and Tutton, C. J. 1891).

Vapour density determinations show that the gaseous molecule of the oxide has the formula P_4O_6. Determinations of the molecular weight by Raoult's method give similar results.

Phosphorus tetroxide P_2O_4 was first obtained by Thorpe and Tutton (C. J. 1886, 833) by heating the mixed oxides obtained by the slow combustion of phosphorus in a sealed exhausted tube at about 290°. A sublimate of this oxide in clear, transparent, lustrous, colourless, orthorhombic crystals, volatilising at about 180°, is thus obtained. It may be prepared, together with amorphous phosphorus, by heating phosphorous oxide in a sealed tube to about 440°.

This oxide is highly deliquescent and dissolves in water, with evolution of heat, the strongly acid solution being unchanged on boiling. The solution reduces mercuric chloride to calomel on warming, and gives a white precipitate, which rapidly blackens with silver nitrate.

Phosphorous pentoxide, phosphoric oxide, phosphoric anhydride P_2O_5 is the product of the complete combustion of phosphorus. It may be obtained in a state of purity by suspending a porcelain dish, containing burning phosphorus, in a three-necked globe, and drawing dried air through the globe with an aspirator. Two of the necks serve for the entrance and exit of the air, and the third and vertical neck receives a corked tube, through which pieces of dried phosphorus are dropped at intervals into the dish.

Grabowski (A. 136, 119) recommends for the preparation on the large scale the use of a sheet-iron cylinder, having a cover and resting on a sheet-iron funnel. The cover has a chimney closed by a cork, and a damper is fitted to the apparatus so that the air may be admitted as required. The oxide produced is shaken at intervals into a bottle beneath the funnel.

This oxide is a white amorphous powder which, when pure, is perfectly colourless and odourless. It frequently possesses a garlic smell, from the presence of phosphorous oxide, and may have a yellowish colour, more noticeable when a portion is allowed to deliquesce, from presence of the lower oxide P_4O. It rapidly deliquesces, with production of metaphosphoric acid. When added to water, orthophosphoric acid is gradually produced, with evolution of heat. According to Hautefeuille and Perrey (C. R. 99, 33), it exists in three forms, crystalline, pulverulent and vitreous.

Phosphorus pentoxide is the best desiccating agent known, and is largely used in the laboratory for completing the desiccation of gases and liquids, or for removing the elements of water from compounds, as in the preparation of nitrogen pentoxide.

Hypophosphorous acid H_3PO_2 is a monobasic acid whose salts are formed when alkalis or alkaline earths are boiled with phosphorus. The barium salt $Ba(PH_2O_2)_2$ is of most interest, as the acid and salts are usually prepared from it. This salt is formed, with evolution of phosphoretted hydrogen, on boiling phosphorus with baryta water:—$3Ba(HO)_2 + 2P_4 + 6H_2O = 3Ba(PH_2O_2)_2 + 2PH_3$. It may be decomposed by dilute sulphuric acid to obtain the acid, or by the addition of a sulphate to produce another hypophosphite.

Hypophosphorous acid forms a thick syrup, from which crystals melting at 17·4° may be obtained by evaporation below the boiling-point of the solution, and cooling in a freezing mixture. When strongly heated, it decomposes into phosphoretted hydrogen and phosphoric acid. It reduces mercuric chloride to calomel or mercury, and is oxidised to phosphoric acid by chlorine and other oxidising agents. Most hypophosphites dissolve in water, and many in alcohol. They are all powerful reducing agents, and precipitate gold and silver from solution. The sodium salt is used in medicine.

Phosphorous acid $P(HO)_3$ is obtained by the action of water on phosphorous oxide or of moist air on phosphorus. The pure acid may be obtained by the decomposition of phosphorus trichloride with water, or by slowly passing chlorine through a deep layer of phosphorus melted under water—

$$PCl_3 + 3H_2O = P(HO)_3 + 3HCl.$$

On evaporating the solution until it attains a temperature of 180° and forms a thick syrup, it gives on cooling a crystalline mass melting at 70·1° (Thomsen, B. 7, 996). When strongly heated, the acid produces phosphoretted hydrogen and phosphoric acid. The aqueous solution slowly absorbs oxygen. It is a powerful reducing agent, and precipitates gold, silver, and mercury from solution.

Phosphorous acid is tribasic, but, excepting the tribasic sodium salt and some ethereal salts, only two atoms of hydrogen are replaceable by the base. All phosphites are soluble in water, the normal alkaline salts being most soluble. They act as reducing agents similarly to the hypophosphites, but, unlike them, give a precipitate with lime water.

Phosphoric acids. Three acids, produced by the combination of phosphorous pentoxide with one, two, and three molecules of water respectively, are known, their names and composition being as follows: *Metaphosphoric acid* HPO_3 or $P_2O_5.H_2O$; *pyrophosphoric acid* $H_4P_2O_7$ or $P_2O_5.2H_2O$, and *orthophosphoric acid* H_3PO_4 or $P_2O_5.3H_2O$. The sodium salt of a fourth acid $P_4O_7(HO)_6$ or $2P_2O_5.3H_2O$, which may be called tetraphosphoric acid, is also known (Fleitmann and Henneberg, Ann. Chem. Pharm. 65, 324), and Salzer (A. 187, 322) has described a phosphoroso-phosphoric acid or hypophosphoric acid $P_4O_4(HO)_4$, of which phosphorus tetroxide may perhaps be the anhydride. Finally, the sodium salt of *thiophosphoric acid* H_3PSO_3 is known (Wurtz, A. Ch. [3] 20, 472).

Orthophosphoric acid H_3PO_4, usually known as 'phosphoric acid,' is a tribasic acid which is produced when amorphous phosphorus is heated with concentrated nitric acid. The phosphorus slowly dissolves, with evolution of red fumes, and the solution is evaporated in a dish with repeated additions of nitric acid until red fumes cease to be evolved, to ensure the absence of phosphorous acid.

The acid is prepared commercially from bone-ash by digesting 3 parts of the ash with 3 parts of crude sulphuric acid (1·55) and 18 or 20 parts of water for two or three days. The solution, which contains the phosphorus as calcium tetrahydric diphosphate ('superphosphate of lime'), is then pressed in linen filters from the precipitated calcium sulphate, and is concentrated to a syrup, treated with concentrated sulphuric acid to precipitate the lime, and the solution filtered off, evaporated, and ignited to remove the sulphuric acid. By another process the solution is treated with ammonium carbonate, which precipitates the lime and leaves triammonium phosphate in solution. The solution is separated and evaporated, and ignited to expel the ammonia. The acid obtained by either method contains magnesia and other impurities.

In another process the bone ash is dissolved in its own weight of hydrochloric acid of sp.gr. 1·18, diluted with 4 parts of water and 1½ parts of sodium sulphate is added. The filtered solution is neutralised while hot with sodium carbonate, refiltered, and precipitated with barium chloride. The mixture of barium sulphate and phosphate thus obtained is decomposed by sulphuric acid.

Commercial phosphoric acid frequently contains arsenic, either from the phosphorus used or from the acid employed in dissolving the bones &c. The arsenic may be removed by reducing it to the arsenious oxide with sulphurous acid, and precipitating it by passage of sulphuretted hydrogen, after removing the excess of the sulphurous acid by boiling.

To avoid the necessity for removing the arsenic, Wenzell (Proc. Am. Pharm. Assoc. 1882, 556 and Ph. [3] 14, 24) proposes to prepare the acid by the slow, spontaneous oxidation of phosphorus in trays containing a thin layer of water. The phosphorous acid thus produced contains the arsenic as arsenious oxide, which becomes reduced to the elemental state, so that it may be separated by filtration, when the solution is heated to about 190° for half an hour. The filtered solution is oxidised to phosphoric acid by the action of nitric acid. Runyon (Ph. [3] 14, 48) recommends this process, and Sommer (S. C. I. 1885, 574) has described an apparatus for preparing the acid by means of it with greater facility.

To prepare the pure acid the commercial acid may be precipitated as the lead salt by addition of lead acetate, the precipitate being washed and decomposed by subjecting it while suspended in water to the action of sulphuretted hydrogen, or by treating it with dilute sulphuric acid. In the latter case the solution must be evaporated and ignited to remove sulphuric acid, and be then redissolved and freed from traces of lead by means of sulphuretted hydrogen.

Phosphoric acid for medicinal purposes is also prepared by dissolving the pentoxide in water.

By evaporation of its solution *in vacuo* over sulphuric acid, orthophosphoric acid may be obtained in hard, transparent, deliquescent, six-sided ortho-rhombic prisms fusing at 38·6° and losing water at 160°. At about 215° the acid is converted into pyrophosphoric acid, and when heated until dense white fumes commence to be evolved is converted into a highly deliquescent glassy mass of metaphosphoric acid.

The strength of aqueous solutions at 15·5° is shown in the following table (J. Watts, C. N. 91, 160):—

Specific gravity	P_2O_5 in 100 parts	Specific gravity	P_2O_5 in 100 parts
1·508	49·60	1·247	28·24
1·492	48·41	1·236	27·30
1·476	47·10	1·226	26·30
1·464	45·63	1·211	24·79
1·453	45·38	1·197	23·23
1·442	44·13	1·185	22·07
1·434	43·95	1·173	20·91
1·426	43·28	1·162	19·73
1·418	42·61	1·153	18·81
1·401	41·60	1·144	17·89
1·392	40·86	1·136	16·95
1·384	40·12	1·124	15·64
1·376	39·66	1·113	14·33
1·369	39·21	1·109	13·25
1·356	38·00	1·095	12·18
1·349	37·37	1·081	10·44
1·339	36·74	1·073	9·53
1·328	36·15	1·066	8·62
1·315	34·82	1·056	7·39
1·302	33·49	1·047	6·17
1·293	32·71	1·031	4·15
1·285	31·94	1·022	3·03
1·276	31·03	1·014	1·91
1·268	30·13	1·006	0·79
1·257	29·16		

Orthophosphoric acid forms three classes of salts, of which the sodium salts may be taken as types. These include the normal or tri-sodium phosphate $Na_3PO_42H_2O$, the hydric disodic phosphate $HNa_2PO_412H_2O$, and the di-hydric sodic phosphate $H_2NaPO_4H_2O$. The normal alkaline salts are readily soluble and possess an alkaline reaction. The insoluble normal phosphates are converted by dilute acids, even by carbon dioxide, into the soluble hydrogen phosphates. Hydric disodic phosphate and corresponding salts are obtained by adding a solution of the hydrate or carbonate of the base to phosphoric acid until weakly alkaline. The dihydric phosphates of the alkalis are soluble and slightly acid. When strongly heated they produce metaphosphates with evolution of water.

Pyrophosphoric acid $H_4P_2O_7$ is obtained by heating orthophosphoric acid to 215° for sometime. It occurs either as a soft glass or as an opaque crystalline mass. It may be obtained in solution by precipitating the sodium salt with lead acetate and decomposing the precipitate with sulphuretted hydrogen. When heated in solution it is converted into orthophosphoric acid.

Pyrophosphates are obtained by heating the mono-hydrogen phosphates, or by addition of the base to the acid. Both normal and acid sodium and other alkaline pyrophosphates, having an alkaline and an acid reaction respectively, are known. When heated with an acid they are converted into orthophosphates.

Metaphosphoric acid HPO_3 is obtained as a transparent, highly deliquescent glassy mass when orthophosphoric acid is heated until dense white fumes commence to be evolved. It is then known as *glacial phosphoric acid*, and usually contains sodium phosphate, which communicates hardness to the otherwise soft acid (Brescius, Fr. 6, 187, and Bettendorff, *ibid.* 27, 24).

It is also obtained by the spontaneous deliquescence of phosphorus pentoxide.

Metaphosphoric acid volatilises at a bright-red heat. Its salts are prepared by neutralising the acid or by heating a dihydric orthophosphate. Among the salts no less than five modifications are known. They may be regarded as salts of polymeric metaphosphoric acids, and are respectively known as mono-, di-, tri-, tetra-, and hexametaphosphates.

Detection and estimation of phosphoric acid. Ortho-, pyro-, and metaphosphoric acids, or their soluble salts, may be distinguished by the fact that silver nitrate gives a yellow precipitate with the first and a white precipitate with the others. Albumen gives an abundant white precipitate with metaphosphoric acid or with acetic acid solutions of its salts, but gives no precipitate with orthophosphoric and pyrophosphoric acids. Metaphosphoric and pyrophosphoric acids give no precipitate with ammonium molybdate when quite free from orthophosphoric acid.

Pyro- and meta- phosphoric acids are converted into orthophosphoric acid before estimation. Other phosphorus compounds are converted into the same acid by treatment with nitric acid before estimation.

For estimating phosphoric acid, the solution, whose bulk should be as small as possible, is rendered strongly ammoniacal and treated with magnesia mixture—*i.e.* with a mixture of magnesium sulphate or chloride with ammonia and ammonium chloride. The liquid is allowed to stand for 12 hours, and is then filtered and washed with dilute ammonia (1 to 5) until the washings give no precipitate with barium chloride or silver nitrate. The precipitate is ignited, gently at first, and finally over the blowpipe, for 15 minutes, and is weighed as magnesium pyrophosphate $Mg_2P_2O_7$.

The filter-paper should be incinerated separately, after careful separation from the precipitate to prevent reduction of the phosphate. An approximate correction for the error introduced by the solubility of the precipitate may be made by adding ·0005 grm. to the weight of pyrophosphate obtained for each 100 c.c. of washings.

When the substance contains small quantities of iron and alumina its precipitation with the phosphate may be prevented by the addition of excess of citric acid; but in such cases, especially when much iron is present, the molybdate method is preferable.

In this method the solution—which should contain as little hydrochloric acid or chlorides as possible—is acidulated with nitric acid, treated with ammonium molybdate, and evaporated to a small bulk on the water-bath, with addition of more molybdate at intervals until no further *yellow* precipitate is obtained.

The precipitate is filtered off and washed with ammonium molybdate or strong ammonium nitrate solution, and is finally dissolved in the minimum quantity of hot dilute ammonia, treated with a little citric acid, and precipitated with magnesia mixture, as above.

PHOTOGRAPHIC VARNISH *v.* VARNISH.

PHOTOGRAPHY. *Introduction.*—Photography is the art by means of which images of various objects may be formed by specially constructed lenses on sensitive films, and may be there rendered visible and permanent by certain chemical processes.

The word itself is derived from the Greek indicating 'writing or delineating by light'; the light so acting on certain substances as to produce in them changes in their composition which may be rendered visible by the further action of reagents brought in contact with them. The chemical theory involved in these changes is shortly discussed in a later portion of this article.

To describe fully the history and development of photography would be impossible in the present place, and this description will be strictly confined to those points which bear more particularly on the modern development of the art.

The effect of light in changing the nature of chemical substances, more especially certain salts of silver, was known to the ancients, but no use of such changes was made till the experiments of Scheele first demonstrated the action of the solar rays on these salts. He was quickly followed in his experiments by Count Rumford and Ritter, who showed that these actions were produced chiefly by invisible rays; but no practical use was made of the discovery of this action of the light till Thomas Wedgwood in 1802 published his method of producing sun-pictures on white paper impregnated with a salt of silver.

Daguerre and Niepce, taking advantage of the camera obscura invented by Baptista Porta, finally succeeded in rendering the images produced by its lenses permanent; and from a long series of experiments devised the process of the Daguerrotype. To Niepce, however, is due the credit of being the first to notice, and fully establish the fact, that the action of light was capable of rendering bitumen insoluble in its ordinary solvents, and consequently that by placing a drawing which had been varnished to make it transparent over a plate covered with a thin layer of bitumen, and exposing the whole to the sun, the parts uncovered by the lines of the drawing could be dissolved away by certain solvents. It is interesting to remember that these experiments conducted by Niepce have laid the foundation of that method of producing copies which is now known under the name of Heliography or Collotype. A period now followed in which many experiments conducted by Wedgwood, Herschel, and others were carried out on silver compounds, but they proved unsuccessful, chiefly owing to the inability of the experimenters to render the copies made with the silver salts fixed or permanent. Some years afterwards Herschell pointed out that sodium hyposulphite might be used as a fixing agent, and the employment of this substance is retained at the present day. By the association of Niepce and Daguerre, experiments were carried out in the direction of the employment of silver iodide as the sensitive material, these experiments resulting in the final perfecting of the Daguerrotype. In this process a silver plate is treated with iodine, and exposed to the light in the camera. After exposure it is placed in a properly-constructed box and developed by the vapour of mercury. By perfecting his process Daguerre was able to produce a moderately-sensitive film, and many of the portraits done by the Daguerrotype process still exist in a remarkably perfect condition.

About the same time Fox Talbot introduced the process originally called by his name, the Talbotype, in which iodised paper treated with a silver salt was employed. This paper was much more sensitive than the materials employed before, and the exposure necessary was much shortened by development of the image with gallic acid. These pictures were originally termed 'negatives' by Talbot, as the lights and shadows were reversed; so to produce a positive from these a second sheet of sensitive paper was exposed under the negative. We have thus in the works of Talbot the basis of the more modern processes, and the names of 'positive' and 'negative' introduced by him are retained at the present time.

Although minor inventions and improvements succeeded the introduction of the Talbotype, they were entirely overshadowed by the introduction of the 'wet collodion process' by Scott Archer in 1851, which reduced the exposure necessary to a much shorter time, and presented many other advantages which the earlier processes did not possess. As a description in detail of the manipulations necessary in carrying out this process is given, it will suffice here merely to say that the process differed from the Talbotype in employing glass as a substratum for the sensitive material, and coating this with collodion containing the soluble halogen salts which, coming in contact with a solution of silver nitrate in a bath, formed by double decomposition the sensitive compound on the film. This sensitive plate, being transferred to the camera, was exposed to the light, and the invisible image so produced was developed in the dark room in a manner afterwards to be described.

For a long time the wet collodion process held its own; but gradually the advantages to be obtained from a plate sensitised in some way which would enable it to keep without deterioration for some length of time began to make themselves felt, and the processes for obtaining such plates either with a collodion or gelatine emulsion have supplanted to a great extent the wet plate process. At first the dry plates in use consisted of those prepared in the silver bath, which, after being sensitised and washed, were dipped in some preservative material capable of retaining the sensitiveness of the film for considerable periods. These, however, rapidly gave place to the process now in use, where the sensitive salts are mixed with warm solutions of gelatine and spread upon the glass plates. When dry the plates are ready for use, or they may be stored, and will apparently keep in a perfect condition for a long period of time. These modern plates differ from the older form of wet plate in being from 10 to 100 times more sensitive, and have thus rendered possible the photography of moving objects and of those which are only dimly lighted.

In 1871, Dr. R. L. Maddox produced some successful photographs with gelatine emulsion, and a little later they were commercially prepared and introduced for sale by Mr. R. Kennett and Mr. Burgess. A still more sensitive emulsion was devised by Mr. Bennett about 1878, which was produced by prolonged digestion of the prepared mixture at 32°C., and finally the discovery that the finished emulsion could be rendered still more rapid by boiling for a short time, or in certain cases by the employment of ammonia in its formation, has given us the numerous and rapid plates which are now to be procured.

Apparatus employed.—For a full description of the various forms of apparatus employed in photographic work, the reader must consult the text-books, it being impossible in the space of this article to go fully into such matters. There are, however, two important pieces of apparatus—the lens, and the camera—about which a short description may be given.

The lenses in general use for photographic purposes may for convenience be grouped in the following classes: (*a*) single lenses; (*b*) rapid rectilinear; (*c*) wide angle rectilinear; and (*d*) portrait lenses. In all cases, although the first have been termed 'single lenses,' it must be understood that photographic lenses are combinations of two or more simple lenses, and the term 'single lens' here refers to the fact that only one combination is used, instead of two or more, as in the other or more perfect lenses.

The single lens consists generally of a combination of two converging meniscus lenses separated by a diverging meniscus, arranged as a combination in the tube of the lens at the end nearest the camera; the convex side of the combination being towards the plate. This is a lens with which it is best to begin photographic work, and in many respects is a most useful lens. It is fairly rapid with a moderately wide angle, and gives good definition. It is not, however, applicable for the photography of large buildings near at hand, as the marginal rays suffer distortion.

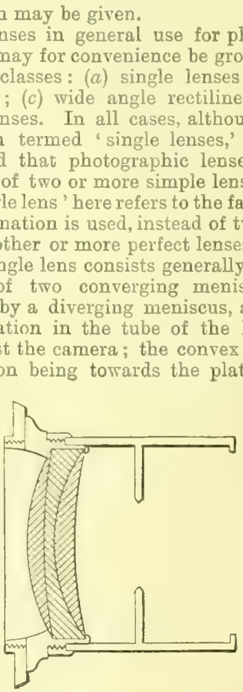

Fig. 1.—Single Lens.

A rectilinear or symmetrical lens consists of two combinations, arranged at the ends of the brass tube, front and back. These combinations are the same in both cases, consisting of a converging meniscus lens cemented to a diverging meniscus, the latter occupying the outside positions in the tube. This is a useful lens,

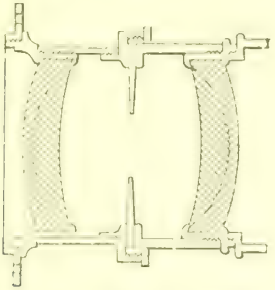

FIG. 2. RAPID RECTILINEAR LENS.

giving practically no distortion and possessing a fairly wide angle.

A symmetrical but wide angle lens is constructed much in the same way, and has two combinations formed of meniscus lenses but of much deeper curvature than those employed in other combinations, and placed closer together in the lens tube. Such lenses take in a very

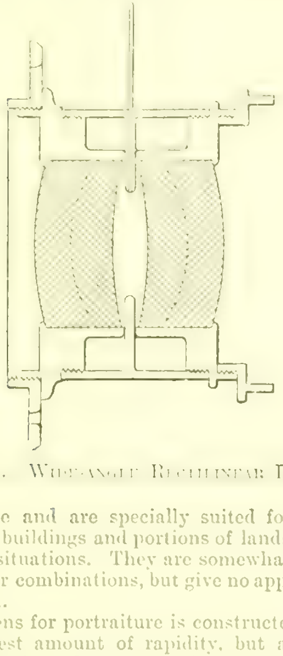

FIG. 3. WIDE-ANGLE RECTILINEAR LENS.

wide angle and are specially suited for photographing buildings and portions of landscape in cramped situations. They are somewhat slower than other combinations, but give no appreciable distortion.

The lens for portraiture is constructed to get the greatest amount of rapidity, but although possessing that advantage it has some defects. It consists of a back and front combination arranged at some little distance apart. The front combination contains a double convex and a plano-concave lens cemented together, the double convex lens taking the position next the object; the back combination consists of a double convex and a diverging meniscus lens, which are frequently mounted so as to leave a small space between the two lenses. The double convex lens is placed in the tube in the position next the camera.

With the dry plates now obtainable great rapidity can be got with this lens, but it has little depth of focus, has poor marginal definition, and presents a rounded field. It is devised for portraiture, and is well adapted for that purpose.

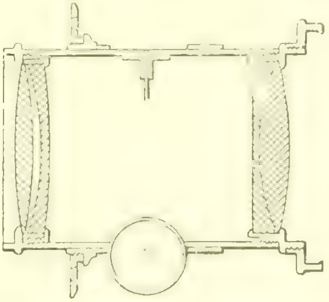

FIG. 4. PORTRAIT COMBINATION.

In some of the newer lenses constructed on this principle great improvements have been made, diminishing these disadvantages and rendering the lenses useful as universal lenses capable of adaptation to general work.

The Camera.—This consists of a box, made of wood, or, preferably, as in the modern cameras, a framework of wood with a bellows-expanding body of leather, so that when closed the camera may occupy little space and be comparatively light. In the front of the camera is placed the lens, and at the back a plate of ground glass, on which the image of the object to be photographed may be focussed, together with an arrangement for lengthening or shortening the body of the camera. The position of the ground-glass screen is the same as that occupied subsequently by the sensitive plate.

Accompanying the camera are one or more double-backed dark slides, arranged to carry two dry plates each, back to back, with a blackened slip of thin sheet iron between them and a shutter arrangement, so as to expose the plate when in the camera. As many of these slides as the operator wishes may be carried with each camera. In the case of work with wet plates it is customary to use a dark slide holding only one plate. The dark slides of larger cameras may be fitted with light wooden carriers, which allow of smaller plates being used in these cameras. For the exposure of paper coated with emulsion in the camera other arrangements, such as roller slides, are required, on which the paper may be stretched. A description of these will be found under the section describing paper negatives and stripping films. The camera should be made of light and well-seasoned wood, and the body of good leather. It should be capable of opening out to a length two or three times as much as the length of the largest plate it carries. The corners may be brass-bound, especially for cameras required in hot climates. The front, in which the lens is screwed, should be provided with a vertical and a horizontal adjustment, so that the position of the lens in these directions may be changed at will without altering the position of the camera; and the back of the instrument should have a certain degree of swing, so that the angle between the sensitive plate and the axis of the lens may be varied when required. The object of raising the front with the lens is to get in high objects and to reduce the amount of foreground, which is frequently too much when the camera is placed horizontally. The swing-back may be employed with two objects: firstly, in the photography of tall buildings with vertical lines, which may be kept moderately parallel by raising the lens slightly, tipping the camera, and swinging the back so that the latter is again brought to the vertical position. Its second use is in the case when it is required to obtain the near foreground in focus as well as the middle distance and that beyond it. If the back of the camera be swung slightly away from the lens it is possible to obtain a considerable improvement in the focussing of the nearer objects without destroying that of those more in the distance. In certain cases cameras are fitted with a side swing, which is used for exactly the same purpose as the vertical swing, only that it is applied to cases where one side of the object is nearer the camera than the other.

To obviate the necessity of dark backs cameras have been designed in which a separate slide for the plates is dispensed with, and its place taken by a multiplex back, containing about eight or more plates, which, by a mechanical arrangement, can be alternately exposed to the light. This multiplex back contains loose wooden frames furnished with light metal screens, and buttons for fastening the gelatine plates in front of the screens. The frames are arranged in two separate tiers, one above the other, one of the tiers containing a fewer number of screens than the other. By turning over the box a frame at once drops down into the vacant space in front of the lower tier, and is ready for exposure to the lens. If this is done, each plate in succession can be brought into position for exposure. The box is provided with a window of red glass, so that the number of the screen in position can be readily seen from the outside. Other more modern cameras of a similar nature have been recently introduced.

The support for the camera should be as strong and steady as possible consistent with lightness. For out-door work the camera stand is generally made to fold up, so as to make it more portable, and in most cases the legs of the stand have a sliding adjustment, which is a matter of some importance when working on unequal ground. The most important requirement of a stand is perfect rigidity when fixed, so that no vibration may be communicated to the camera during exposure.

Action of light on silver compounds.—Although many chemical substances undergo change under the influence of light, the halogen compounds of silver are those generally employed in photography, and they may be conveniently taken to illustrate such changes, as well as those taking place in the further processes of development and intensification.

With regard to the formation of the latent image, it is right at the outset to say that we have no absolutely definite knowledge of the composition of that image. It is generally accepted, however, that the change, so far as the halogen silver salts are concerned, is the conversion of these into sub-salts, as may be shown by silver bromide, $2AgBr = Ag_2Br + Br$, this change being common to the three halogen salts. Recent experiments of Carey Lea have, however, shown that the change is probably of a much more complicated kind. Whatever the exact nature of the change may be, there is quite sufficient evidence to show that it will not take place with any facility unless some agent is present which will absorb the halogen as it is liberated during the change. Such agents are to be found in certain metallic salts and in organic substances. In the wet collodion process the presence of excess of silver nitrate on the surface of the sensitive plate acts as such an absorbent. To trace the extent to which such silver compounds, either alone or when mixed, are sensitive to the action of light, the examination must be made by photographing the solar spectrum. This has been extensively done by Abney, Vogel, and many others, and the following general conclusions may be drawn from the experiments:—

The action of the light is different for each of the halogen salts of silver, either alone or when mixed.

It differs also according to the material with which the sensitive compound may be mixed or on which it may be spread, whether at the time of exposure to light the material be in a moist or in a dry condition and, finally, the different quantities in which the sensitive compounds may be mixed together.

Chemical action in development of the image.—As the action of light would have to be immensely prolonged to produce a visible image on the sensitive film, reagents are employed which, exercising a reducing action on the silver salts, carry on and render visible the action begun by the light. Such agents are termed developers, and the actions which they perform may be described under two headings: (1) acid development, and (2) alkaline development.

The action in the first case is that which takes place in the development of wet collodion plates, and may be illustrated by the action of ferrous sulphate on silver nitrate, $6AgNO_3 + 6FeSO_4 = 2\{Fe_2(SO_4)_3\} + Fe_2(NO_3)_6 + 3Ag_2$, in which it is assumed that the silver so deposited adds itself to the silver salt already changed by the action of the light, and decomposed by the developer, thus:

$$2Ag_2Br + 3FeSO_4 = Fe_2(SO_4)_3 + FeBr_2 + 4Ag.$$

The developed image, therefore, is essentially on the surface of the film, because the silver salt is on top of the film. If the ferrous salt and silver nitrate be brought together alone too rapid reduction may take place. It is customary, therefore, to employ certain substances which act as restrainers during the decomposition. These are to be found in acids, either mineral or organic, and in certain other organic compounds.

Besides iron salts, pyrogallic acid is employed, both in the wet-collodion and in the dry-plate processes, the action here, as in the first case, being one of reduction of the silver salt in the presence of some halogen absorbent. In alkaline development the reducing or developing action takes place generally on silver subbromide first, produced by the action of light on the bromide, the bromine, which has been set free, being absorbed by the organic substratum. In this development the change is generally produced by pyrogallic acid, rendered alkaline by ammonia or some other alkaline substance, the acid alone being unable to effect the reduction of the sub-bromide to metallic silver. In the presence of an alkali, however, it becomes a rapid absorbent of oxygen, or of an equivalent of chlorine, bromine or iodine.

As there seems reason to believe that freshly-deposited silver converts unaltered silver bromide into the sub-bromide, and as this sub-bromide, on being attacked by the developer, would at once give a deposit extending over the plate farther than the area of the action of the light, it is necessary to have with the developer some substance capable of acting as a restrainer on the secondary decomposition. Generally, soluble bromides are employed for this purpose, and it is possible that they form a double salt with the silver bromide, which is less easily attacked by the nascent silver, so obviating a deposit except when the light has begun the action.

Development may also be carried out with organic salts of iron, of which the most important is ferrous oxalate. In this we have the conversion into ferric oxalate during the process: $2Ag_2Br + 3(FeC_2O_4) = Fe_2(C_2O_4)_3 + FeBr_2 + 4Ag$, a change comparable with that of the ferrous sulphate already spoken about.

It must be understood that our present knowledge of the action of light and of developers on silver salts is not complete enough to enable equations to be written exactly expressing the changes which occur.

[illegible] intensification [illegible].—In the process of intensification we have virtually a strengthening of the developed image, which may be brought about in two ways: either by causing a further deposition of silver, or a deposition of some other substance on the silver already deposited during development.

For the first case the change is analogous to that of development; as an instance of the second the following may be taken:

$$Ag_2 + 2HgCl_2 = Hg_2Cl_2 + 2AgCl, \text{ and}$$

$$Hg_2Cl_2 + 2NH_4OH = NH_2Hg_2Cl + NH_4Cl + 2H_2O,$$

when in the first place the silver deposited on the plate, on treatment with mercuric chloride, yields mercurous and silver chlorides. On application of ammonia solution to this, after washing, we have the image darkened by the formation of black dimercurous-ammonium chloride.

Other intensifying agents are employed, of which the following are the most important:—Mercurous chloride, after washing with sodium sulphite,

$$Hg_2Cl_2 + Na_2SO_3 + H_2O = 2Hg + Na_2SO_4 + 2HCl.$$

Mercurous chloride with ferrous oxalate,

$$Hg_2Cl_2 + 2AgCl + 4FeC_2O_4 + 2K_2C_2O_4$$
$$= 2Hg + Ag_2 + 2Fe_2(C_2O_4)_3 + 4KCl.$$

Potassio-silver cyanide on mercurous chloride,

$$Hg_2Cl_2 + 2AgK(CN)_2 = Ag_2 + 2Hg(CN)_2 + 2KCl.$$

The ferricyanides of lead or uranium on the silver image, $2Ag_2 + 2Pb_3Fe_2(CN)_{12}$

$$= Ag_4Fe(CN)_6 + 3Pb_2Fe(CN)_6.$$

The substances formed in this case, being white, are, after washing, treated with an alkaline sulphide to convert them into the dark sulphides. The ferrocyanide of uranium, possessing a dark brown colour, renders the picture sufficiently dense without further treatment.

Fixing the negative.—This is generally done with sodium hyposulphite (thiosulphate) or potassium cyanide. The action of these substances depends upon the formation of double salts of silver with the alkali metals, which are soluble in water, and which can be washed away from the negative. In the case of fixing by sodium hyposulphite, it is necessary that the solution should be concentrated, otherwise an insoluble double salt may be produced. The action in each case may be represented by the following equations:

$$AgBr + 2KCy = AgKCy_2 + KBr$$

$$2AgBr + 3Na_2S_2O_3 = Ag_2Na_4(S_2O_3)_3 + 2NaBr.$$

Reducing negatives.—It often happens that a negative may become too dense during the process of development, and it is then necessary to reduce its density. This may be done either by mechanical or chemical means, the latter being preferable. In the application of chemical means two actions may take place, (1) the image may be converted into one of another or less dense colour, or (2) the excess of silver deposit may be removed; this is by far the best course, and is done by transforming the silver into the chloride or bromide of silver, and removing that by solution. Many substances effect this change, such as cupric and ferric chlorides, bleaching powder solutions, sodium and potassium hypochlorites. The silver reduces these salts, becoming itself converted into chloride, which may be removed by again fixing.

With copper and ferric chlorides we have

$$Ag_2 + 2CuCl_2 = 2AgCl + Cu_2Cl_2$$

$$Ag_2 + 2FeCl_3 = 2AgCl + 2FeCl_2.$$

These methods have the disadvantage of not showing the full diminution in density till the whole of the AgCl has been removed by the fixing agent. To allow of the final reducing action being seen during the operation, a process has been introduced by which potassio-ferric oxalate is simultaneously used with the sodium hyposulphite

$$Ag_2 + Fe_2(C_2O_4)_3 = Ag_2C_2O_4 + 2(FeC_2O_4)$$

$$Ag_2C_2O_4 + 3(Na_2S_2O_3) = Ag_2Na_4(S_2O_3)_3 + Na_2C_2O_4$$

(Eder). Potassium ferricyanide may also be employed with sodium hyposulphite

$$2Ag_2 + 2K_6Fe_2(CN)_{12} = Ag_4Fe(CN)_6 + K_4Fe(CN)_6.$$

$$Ag_4Fe(CN)_6 + 6Na_2S_2O_3$$
$$= 2\{Ag_2Na_4(S_2O_3)_3\} + Na_4Fe(CN)_6.$$

[illegible] [illegible] glass plates for coating—either with collodion in the wet-plate process, or for the more modern processes with emulsions—it is necessary, if they have been used before, that all the old film should be removed; and whether they have been used or not, to polish them so as to receive the fresh coating. The old films may be removed by soaking the plates for twenty-four hours in solutions of hydrochloric or nitric acids containing 1 part of the acid to 20 parts of water. After this time the film can be easily removed by brushing with a nail brush and warm water. After removal of the film the plate should then receive a polish, so that the coating may flow easily over the surface. This is best done with ordinary whiting and water made up to a creamy consistency, or, what has proved very effectual in the writer's experience,

rouge made up to the same consistency with alcohol, and a few drops of ammonia added to it to dissolve grease stains. The plate having been laid down on a pad of thick flannel, a little of the fluid containing the rouge is poured on the plate, which is then gently rubbed with a small pad of flannel. The alcohol gradually evaporating leaves the plate covered with a thin film of dry rouge, which is best removed by gently polishing with a pad of tissue paper, the final polish to the plate being given with a second pad. If whiting and water are used, the powder, when dry, must be removed with a slightly-damped cloth, and, however perfect the cloth may be, it is apt to leave shreds on the surface of the plate, which may be obviated by using the tissue paper.

When cleaned, it is customary to give the plate an edging or substratum of some material which will assist the collodion or the emulsion to stick more firmly to the plate during the subsequent processes of washing, &c. In the case of dry plates it is not always absolutely necessary to employ an edging, but it is sometimes advisable, and is almost imperative with collodion films. Many substances are employed, but the following solutions will be found sufficient for substrata :—

—	*a*	*b*	*c*	*d*	*e*
Albumen	White of 1 egg	Dried 50 grs.	—	—	—
Gelatine	—	—	75 grs.	—	—
Ammonia	5 mm.	5 mm.	2 drs.	—	—
India-rubber . . .	—	—	—	5 grs.	5 grs.
Chloroform . . .	—	—	—	5 ozs.	—
Benzole (rectified) . .	—	--	—	—	5 ozs.
Water	60 ozs.	50 ozs.	60 ozs.	—	—

a and *b* must be filtered before use through a light plug of cotton-wool. The albumen in *b* may be dissolved in water at a temperature not exceeding 49°C. In *a*, *b*, and *c* the plates may be immersed entirely in the solution, and then placed on the rack to dry. In *d* and *e* the solution should be poured on as described for coating with collodion, or an edging of about a quarter of an inch may be given with a brush. It is advisable to edge both sides of the plate, as this facilitates work afterwards in the dark room.

THE COLLODION PROCESS.

The development of the more rapid modern processes of photography may be said to date from the introduction of this process by Scott Archer in 1851. The process depends upon the coating of glass plates with a stratum of soluble pyroxyline or collodion, impregnated with soluble iodides or bromides, which form the sensitive silver compound when placed in a solution of silver nitrate.

The soluble pyroxyline or collodion cotton $C_{18}H_{21}O_6(HO)(NO_3)_8$ is formed by the action of a mixture of nitric and sulphuric acids with a little water (HNO_3 with H_2SO_4 and $1\frac{3}{4}H_2O$), or of a mixture of potassium nitrate with sulphuric acid upon cotton. It differs from cotton in being soluble in a mixture of alcohol and ether, yielding a viscous fluid, which on evaporation leaves the pellicle or film of collodion.

To prepare the soluble cotton for collodion, 3 measured ounces of nitric acid (sp.gr. 1·429) are mixed with 2 ounces of water in a pint beaker. Nine measured ounces of strong sulphuric acid (sp.gr. 1·839) are then added to this mixture with constant stirring, and the mixture allowed to cool to 60°C. 100 grains of dry cotton, in tufts of about 10 grains each, are immersed in the mixture of acids and allowed to remain from five to ten minutes in a covered beaker. The acid is then poured off, the cotton squeezed with a glass-rod, washed in a stream of water till all acid has disappeared, and finally dried by exposure to the air. Before drying, the cotton may be washed with a little weak solution of sodium carbonate to ensure the total removal of the acid.

The cotton employed must be entirely cleansed of all resinous matter adhering to it, and for this purpose it should be well boiled in sodium carbonate, then thoroughly washed, and finally well dried before immersion in the mixed acids.

For larger quantities of pyroxyline the following amounts of the different acids may be taken :

	a	*b*
Sulphuric acid, sp.gr. 1·845	18 ozs. fl.	18 ozs. fl.
Nitric acid, sp. gr. 1·457 .	6 „	6½ „
Water	4¾ „	4¼ „

The nitric acid is first added to the water, and lastly the sulphuric acid, the mixture being well stirred and allowed to cool. These quantities of acid will convert about 360 grains of cotton.

For the manufacture of pyroxyline by the second method with potassium nitrate, the following quantities will be found useful :

Sulphuric acid . . .	6 ozs. fl.
Dried potassium nitrate . .	3½ ozs. (av.)
Water	1 oz. fl.

The acid and water must first be mixed together, and the dried potassium nitrate then added gradually when in a finely-crushed condition. On stirring, a transparent viscous liquid is obtained, which must be kept at a temperature of 52°C. Into this about 60 grains of dried cotton are then dipped in the manner previously described, and allowed to remain in the mixture for ten minutes.

In both processes the pyroxyline when dry should break up easily, tearing readily in the hand.

To form collodion from pyroxyline, it is dissolved in a mixture of alcohol and ether, which for ordinary work may be taken in the following quantities :

	a	*b*
Pyroxyline . .	55 to 65 grs.	55 to 65 grs.
Alcohol (·820) .	4½ ozs.	5 ozs.
Ether (·725) .	5½ ozs.	5 ozs.

a may be taken for work in winter; *b* for work in summer.

When plain collodion has been prepared it is then necessary that it should be iodised so as to form the sensitive silver salt when placed in the silver bath. The iodides and bromides in general use are those of the metals zinc, cadmium, potassium, and ammonium, the two last being those most frequently employed. The following numbers give in a tabular form the quantities of the different salts which may be employed for iodising 1 oz. of plain collodion:—

—	*a*	*b*	*c*	*d*
Plain collodion	1 oz.	1 oz.	1 oz.	1 oz.
Cadmium iodide		2 grs.	½ gr.	
Cadmium bromide	2 grs.	2 grs.	—	[illegible] grs.
Ammonium iodide	3 grs.	1 [illegible]	3 grs.	[illegible] grs.
Ammonium bromide	—	—	1 [illegible]	

a should be mixed some weeks before use, and is suitable for landscapes; *b* may be used for portraiture; *c* forms a good collodion for general use, and may be used a day or two after mixing; *d* is a good ordinary collodion. If simply an iodised collodion is required, then 4 grains of ammonium iodide, or 5 grains of cadmium iodide, may be added to the ounce of plain collodion; the first is used immediately after iodising, the second requires keeping. Although it is customary to dissolve the pyroxyline and the soluble iodides and bromides separately in the alcohol and ether, this is not absolutely necessary, and the collodion may be formed equally well by dissolving the iodides and bromides in the liquid in which the pyroxyline has already been dissolved.

For making larger quantities of collodion the following quantities will be found useful:—

—	*a*	*b*	*c*
Pyroxyline	120 grs.	120 grs.	100 grs.
Ether (·725)	10 ozs.	10 ozs.	10 ozs.
Alcohol (·805)	[illegible] ozs.	10 ozs.	10 ozs.
Ammonium iodide	12 grs.	40 grs.	—
Ammonium bromide		—	20 grs.
Cadmium iodide	20 grs.	40 grs.	50 grs.
Cadmium bromide	—	20 grs.	-

a is for negatives; *b* for negatives; and *c* for positives and ferrotypes.

The [illegible] employed in the manufacture of this bath is invariably silver nitrate, and the strength for the ordinary silver bath is from 35 to 40 grains of silver nitrate to the ounce of water; in certain cases, however, the strength may rise to 50 grains to the ounce, but this is too great for ordinary purposes. About ⅛th grain of potassium iodide should be added for every 40 grains of silver nitrate; or the bath may be allowed to become saturated with iodide of silver during the subsequent working.

To make the bath, from a quarter to half the quantity of water to be employed is taken, and in it the silver nitrate is dissolved; to this solution is added the quantity of soluble iodide, which will cause a precipitate of silver iodide gradually dissolving on shaking. Next add the remainder of the water, allow to stand, and then filter. After preparation the bath should be slightly acid, and for this a drop or two of nitric or acetic acid may be added, preferably the former. Should the bath be too acid after making, a little sodium carbonate may be added. The following are convenient quantities for the preparation of larger amounts of bath solution:

	[illegible]	[illegible]
Silver nitrate (recrystallised)	6 ozs.	5 ozs.
Distilled water	80 ozs.	80 ozs.
Nitric acid	10 mm.	12 mm.

Saturate with an iodide as before described, and filter.

Development of the latent image.—The chemistry of the action taking place in this process having been indicated in an earlier portion of the article, it is only necessary now to give some of the formulæ best adapted for the development of the image. Those which follow relate more particularly to the wet or collodion process, and belong to the first division of the phenomena connected with development—viz., to acid development.

The following table gives the quantities necessary for some useful iron developers for wet plates:—

—	*a*	*b*	*c*	*d*	*e*	*f*	*g*
Ferrous sulphate	50 grs.	150 grs.	250 grs.	100 grs.	—	100 grs.	100 grs.
Glacial acetic acid	75–100mm.	[illegible]	100 mm.	100 mm.	125 mm.	90 mm.	[illegible]
Alcohol	quant. suf.	suf.	suf.	suf.	suf.	[illegible]	suf.
Water	5 ozs.	5 ozs.	5 ozs.	5 ozs.	5 ozs.	5 ozs.	5 ozs.
Copper sulphate	—	—	—	50 grs.	—	—	—
Ammonio-ferrous sulphate	—	—	—	—	125 grs.		—
Sugar	—	-	-	—	—	[illegible]	
Gelatine	—	—	—	—	—		5 grs.

a may be used in moderate light; *b* when great contrast exists in the lights and shades; *c* where under-exposure is feared; *d* for landscape work. These developers are applicable to negatives only. The following may be employed—*a* for positives and ferrotypes; *b* for positives:

Ferrous sulphate	[illegible]	[illegible]
Barium nitrate	[illegible]	—
Pyrogallic acid	—	5 grs.
Acetic acid	—	[illegible]
Alcohol	[illegible]	sufficient
[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]

In wet-plate work the development, as a rule, is carried out by pouring a sufficient quantity of the fluid over the plate. The plate being held as described for coating with collodion, the fluid is run gently and steadily over it, care being taken not to pour the developer always on one spot. The liquid is then allowed to flow backwards and forwards over the plate with a rocking motion, whilst the image gradually appears.

When sufficient detail has made its appearance, the excess of developer is washed off by a stream of water.

With new baths little alcohol is required in the developer, but more must be added when the bath has been some time in use to make the liquid flow freely over the plate.

Intensification of wet plates.—When the density of the negative is not sufficient for printing purposes, it may be strengthened by pouring over the plate a sufficient quantity of either of the following solutions:

	a	*b*
Pyrogallic acid . .	10 grs.	—
Citric acid . .	20 grs.	50 grs.
Ferrous sulphate .	—	25 grs.
Water . . .	5 ozs.	5 ozs.

After the plate has been thoroughly moistened with the solution, the latter should be poured back into the developing-glass and a few drops of a 10-grain solution of silver nitrate added to it. On re-flooding the plate with the mixture, the image will gradually gain in density. Other substances may be employed as intensifiers, some of which will be mentioned in connection with dry plates, but for a full description of the various formulæ text-books on photography must be consulted.

Fixing.—To remove the unacted-upon silver salt, either sodium hyposulphite (thiosulphate) or potassium cyanide may be employed; the solution being contained in a flat dish, or in an upright bath provided with a dipper. The following quantities are those generally employed:

	a
Sodium hyposulphite . .	4 ozs.
Water	20 ozs.

	b
Potassium cyanide . . .	120 grs.
Water	5 ozs.

a is preferred for negatives, *b* for positives. Great care is required in the employment of the latter salt on account of its very poisonous character.

Varnishes.—For the protection of the collodion film it should be covered with a coating of varnish as clear and as hard as possible, to prevent damage during the operation of printing. These varnishes are resins dissolved in such solvents as alcohol, benzole, or chloroform. The composition of some of these is kept secret, but the quantities given in the next column yield good material for ordinary work.

a and *c* are suitable for negatives, *c* being very hard and durable. *b* may be rubbed off for retouching the negative, and should not be used when great permanency is required. For further details with regard to photographic varnishes *v.* Varnish.

—	*a*	*b*	*c*	*d*
Shellac . . .	300 gr.	—	—	—
Sandarac . .	300 gr.	384 gr.	—	430 gr.
Mastic . . .	120 gr.	—	—	—
White hard varnish	—	—	3 oz.	—
Camphor . .	5 gr.	—	—	—
Oil of lavender .	—	5 dr.	—	1 dr.
Chloroform . .	—	1 dr.	—	—
Oil of turpentine .	1 dr.	—	—	3 dr.
Venice turpentine .	1 dr.	—	—	—
Alcohol . . .	10 oz.	5 oz.	5 oz.	5 oz.

Dry Plate Processes.

Collodion emulsion.—Next to the wet plate process just described we come to the more modern or emulsion processes, which may conveniently be divided into those containing collodion and those containing gelatine as the thickening material in the emulsion. Those formed with gelatine are now the most important, but, the others being useful for certain purposes, we will briefly describe the production of a collodion emulsion before proceeding to that in which gelatine is employed.

The plates having been prepared and edged as previously described in the wet-plate process, they may be coated with an emulsion prepared in the following manner. The plain collodion may be made by dissolving 200 grains of ordinary pyroxyline in 5 ounces of alcohol (sp.gr. ·820) mixed with 10 ounces of ether (sp.gr. ·730). To make, say, 1 pint of emulsion from this, after the final treatment of emulsification, drying, washing, and re-emulsifying has been gone through, we may take 7½ ounces, or the half of the collodion prepared. 200 grains of zinc bromide are next weighed out in two portions of 100 grains each, one of these portions being dissolved in the smallest quantity of alcohol, 4 or 5 drops of nitric acid added to it, and then poured into the collodion. The second 100 grains are dissolved in a boiling tube in alcohol, 10 drops of nitric acid added, and kept ready for use. Next 330 grains of silver nitrate are weighed out and dissolved in about 5 to 6 dr. of water, and 10 drops of nitric acid added to the solution. To this solution 1½ ounces of warm alcohol are then added, and the two liquids thoroughly mixed. The collodion containing the zinc bromide is now placed in a vessel convenient for mixing, and the solution of silver nitrate gradually added, with constant stirring, till about one half to three quarters of the silver solution has been poured in. The whole of the bromide solution is now added in exactly the same way as described, and then the remainder of the silver solution. Should any of the silver solution crystallise on the sides of the boiling-tube it may be dissolved in a little water and about half an ounce of alcohol, and added to the emulsion with constant stirring. The emulsion so prepared, when examined by a candle or gas flame, should appear of a deep orange tint by the light transmitted through a thin film.

Manufacture of gelatine emulsions.—Of these emulsions several are before the public, differing from each other in their condition of rapidity. To save space, a table is given further on, containing the quantities employed in certain standard formulæ, and therefore short instructions only are now given for the preparation of a gelatine emulsion which may be taken as generally applicable to all.

It is necessary that all the operations of making the emulsion—heating to obtain the required rapidity, and finally washing the emulsion when formed—should be carried out in the dark room or in red light. For most cases light passing through ruby glass is sufficient, but in the manufacture of extra rapid emulsions more precaution with regard to light is necessary. As during the process of manufacture the emulsion must be kept at a certain temperature, glass vessels are necessary for dissolving and mixing the constituents, and a small pan or dish is required for keeping these vessels at the required temperature by hot water. The enamelled dishes used for developing platinum prints will answer the purpose very well, and can be heated by an Argand burner, or, failing gas, with a spirit lamp.

The substances required for a simple emulsion are silver nitrate, potassium bromide, and autotype, or hard gelatine. Convenient quantities for a small amount of emulsion are obtained by taking 300 grains of the gelatine, cut up into shreds by scissors. These are transferred to a glass beaker, or, failing that, to an ordinary jam pot, and covered with 5 ounces of water, in which 185 grains of potassium bromide have previously been dissolved. By a little manipulation with a glass rod the gelatine gradually softens and swells. Whilst the gelatine is being softened, 231 grains of silver nitrate are dissolved in 5 ounces of water by gentle heat in the pan or water-bath, and when the solid is thoroughly dissolved some strong solution of ammonia (·880) is gradually added to the silver solution, with constant stirring, till the precipitate which first forms is dissolved. The two vessels are now placed in the pan with water, which is kept rigorously at a temperature never rising above 35°C. till the gelatine becomes first viscous, and then, with constant stirring, perfectly liquid. It is essential that the gelatine be perfectly liquid before adding the silver salt. Up to this point the operations may be carried out in the ordinary light, but all further work must be done in ruby light.

When the gelatine is thoroughly liquefied the solution of silver nitrate is gradually added little by little to the warm gelatinous mixture with constant stirring. Many arrangements have been devised from time to time for the proper addition of the silver solution to the gelatine, but it can be done with ease by pouring the solution in a thin stream from an ordinary lipped beaker, or through a glass funnel with a very small orifice. When the mixture is complete, wash out the rest of the silver solution remaining in the beaker with about an ounce of warm water, and add to the emulsion. The emulsion must now be examined by spreading a little on a glass plate and looking at it by transmitted light, when it should appear of a violet colour, apparently with a tendency to assume a rose-pink tinge. The emulsion having been allowed to remain in the hot water for from half to three quarters of an hour to undergo a process of ripening, it is then poured out into a flat photographic dish, placed in a perfectly dark box, and allowed to set. It should remain thus for at least 24 hours, but will be still better if allowed to remain two or three days. As the emulsion when first prepared contains an excess of silver salt, it must undergo the further and most important process of washing, which may be carried out in two very simple ways—of course, in ruby light.

The gelatine pellicle, having been scraped off from the dish by a bone or glass spatula, is transferred to a square of coarse canvas, such as is used for worsted work, thoroughly wetted to soften it. The corners of the square are gathered together and tied with string, thus inclosing the pellicle in a rough bag. This bag, containing the pellicle, is now placed in a vessel of water of sufficient size, and thoroughly kneaded by squeezing it against the sides of the vessel by means of the spatula. The pellicle is thus squeezed in threads through the canvas, and falls to the bottom of the washing vessel. When the whole of the emulsion has been thus treated, the water is poured off and the pellicle again covered with fresh water, allowed to stand for about five minutes, and the water again poured off, this operation being repeated some six or eight times. It will be found advantageous during the process of washing to tease up the shreds of pellicle, which is best done by using two glass rods. Where a tap and running water can be obtained, the washing process will be much facilitated.

After perfect washing the pellicle is turned out of the washing jar on to a porcelain strainer, covered with a handkerchief, and the excess of water drained away. It may then be swilled with a wash of methylated alcohol, which facilitates drying, and transferred by the porcelain spatula or glass spoon to a suitable jar, covered with a lid, till it is required for coating the plates. Other methods of washing the pellicle have been introduced, such as placing it on a hair sieve after squeezing through canvas, and then washing on the sieve in a stream of water from the rose tap. It is possible that spreading the emulsion on a sieve facilitates the subsequent drying.

A second method for washing the emulsion and removing the soluble salts is to precipitate it with alcohol. This is best done by pouring warm methylated alcohol into the emulsion, with constant stirring, when, on allowing the mixture to cool, the emulsion is found precipitated at the bottom of the vessel. The precipitated emulsion can then be washed in a stream of water, and transferred to a covered pot till required for coating the plates.

The numbers just given will be found convenient for a beginner making an emulsion for the first time, and yield one of moderate rapidity. The following table gives a selected series of emulsions suitable for different purposes. Nos. I. and II. have been introduced by Mr. W. K. Burton, and are of different degrees of rapidity, the first yielding a material suitable for landscapes, when no great rapidity is required; the second deals with an emulsion of greater sensitiveness.

Table of Gelatino-Bromide Emulsions.

—		I.	II.	III.	IV.	V.	VI.
A	Silver nitrate	200 grains	200 grains	400 grains	200 grains	330 grains	462 grains
	Distilled water	3 ounces	3 ounces	7 ounces	3 ounces	3 ounces	10 ounces
	Ammonia (880)	—	—	sufficient to dissolve ppt.	—	—	sufficient to dissolve ppt.
B	Ammonium iodide	—	—	24 grains	—	—	—
	Ammonium bromide	—	—	280 grains	120 grains	200 grains	—
	Potassium bromide	160 grains	165 grains	—	—	—	370 grains
	Gelatine (Nelson's No. 1)	40 grains	30 grains	80 grains	30 grains	218 grains	615 grains
	Hydrochloric acid (1 p.c. sol.)	200 mins.	—	—	—	—	—
	Distilled water	2½ ounces	2½ ounces	5½ ounces	4 ounces	3 ounces	10 ounces
C	Potassium iodide	12 grains	6 grains	—	—	—	—
	Distilled water	½ ounce	½ ounce	—	—	—	—
D	French gelatine	—	—	—	—	218 grains	—
	Hard gelatine	300 grains	250 grains	—	200 grains		—
	Water	4 ounces	3 ounces	—	—	3 ounces	—
E	Methylated spirit	—	—	2½ ounces	—	—	—
	Salicylic acid	—	—	25 grains	—	—	—

In No. I. B and D are allowed to stand till perfectly soft and soaked. All the water is then poured off D, and the gelatine squeezed. The beakers or jam-pots containing A and B are now placed in the pan with hot water, and the temperature raised to about 70°C. A is then gradually added to B in small quantities at a time, with constant stirring or shaking between each addition, and a thorough stirring at the end when all has been added. C is now added, and the solutions again shaken. The pan of hot water is now raised as rapidly as possible to the boiling-point, and kept at that temperature for twenty minutes. At the end of this time the gelatine from D is added, the mixture thoroughly stirred, and the pot with the emulsion then placed in the dark box to set.

In No. II. the chief point to be attended to is that the various solutions should neither be too alkaline nor too acid. The silver solution A should be as nearly as possible neutral to test-paper, and B only feebly acid. If B is strictly neutral it may be made feebly acid by a drop or two of dilute hydrochloric acid. The excess of acidity in A and B, should it exist, may be neutralised by dilute ammonia. With these precautions the details of emulsification are the same as for No. I.

After setting, the processes of straining and washing are the same as already described. The boiling process is complete when the emulsion, viewed by transmitted light, ceases to show a ruby colour, but assumes a blue-grey when in thin layers.

As a rule the quantities of water given in the instructions for making the emulsions are quite sufficient; but, if on again warming to filter the emulsion before coating the plate, it is found too thick, a small quantity of water may be added and the emulsion thoroughly stirred. Before coating the plate the washed emulsion must be melted and filtered; this latter is best done by passing it through a sheet of fine cambric lying in an ordinary glass funnel, or filtering it through a plug of cotton or glass wool in the narrow end of the funnel.

For full details with regard to the manipulation necessary for coating the plates with emulsion the text-books on photography must be consulted. The process may be carried out in two ways, and the coating should always be done over a large flat dish, so that in the case of any of the emulsion dropping off the plate it may be recovered and remelted without deterioration.

The emulsion, melted and kept at a temperature of 43°C. or 110°F. in a lipped beaker or small teapot, may be conveniently poured on the centre of the plate exactly as described for coating a wet plate with collodion, except that more than half the plate must be covered with emulsion, and, instead of the liquid being drained off the plate, only a little of the excess of emulsion is returned to the vessel. After this is done the plate is gently rocked to make the coating spread evenly, and then placed on a level slab of thick glass to set. Instead of holding the plate with the finger and thumb, it will be found preferable to employ a pneumatic plate-holder.

For larger plates another method may be used, and in this case the plate must be laid on a very accurately-levelled stand or tripod. A quantity of emulsion sufficient to cover nearly half the plate is poured on the centre of it; a glass rod about two inches longer than the width of the plate is then grasped between the fingers and thumbs of both hands, dipped into the centre of the pool of emulsion across the plate, and steadily moved first to one end and then to the other of the plate. By a motion of the finger and thumb the rod can be raised a slight distance from the plate, so as to allow the emulsion to coat smoothly, and, by resting the tips of the finger and thumb upon the levelled slab, a guiding motion may be given to the rod. With very large plates it is sometimes the custom to spread the emulsion on the plate by laying the latter on a revolving table and pouring the emulsion on the centre of the plate, the centrifugal motion given by the revolution of the table thus spreading the emulsion from the centre to the edges of the plate. In the larger manufactories many other mechanical arrangements to facilitate rapid coating have been introduced.

When the emulsion is thoroughly set on the plates, they are removed from the level slab to a suitable rack to undergo a thorough drying process. This is most conveniently done in a specially-constructed drying-box with a current of air artificially heated from the outside passing through it. The artificial heating of the air is unnecessary if the air-passages are sufficiently large and properly arranged. There are many varieties of drying-boxes in use, but perhaps the most convenient form for plates of a moderate size is one in which the air enters at the top of the box and is drawn through this into an air chamber at the bottom, thence passing up a large tube or chimney outside the box with a gas-flame burning in it so as to produce the required draught. This tube should be taller than the box, and should be carried into a chimney or into the open air. The plates are placed on racks, drawings of which are given in many of the text-books. The racks may then be placed on cross-rods representing shelves, the heights of which may be altered to suit the different sizes of the plates.

The plates will take from twelve to forty-eight hours to dry, according to circumstances, and may then be packed till required for use. Plates may be packed either face to face with thin slips or tissue paper between them, or preferably in grooved light-tight boxes, which need not be made of wood, but which may be constructed of strong pasteboard and lined with the corrugated material now employed for parcels sent by post. If packed in flat boxes the plates must be packed together in a thickness of opaque orange paper, and then in two thicknesses of brown paper. Not more than twelve plates should be placed in one box, and it will be found convenient to divide that number into three separate packets.

Ortho-chromatic photography.—On comparing the curves indicating the intensities of the visual and the photographed spectrum, it will be at once observed that very little relation exists between them, the visual intensity being greatest about the points D and C, and the photographic intensity about the point G in the spectrum, gradually diminishing to the points marked F and E.

The object of ortho-chromatic photography is by the use of certain dyes introduced into the sensitive material to bring the visual and the photographic intensity as much into harmony as possible. This unison may be partially brought about by the introduction into the photographic film of substances such as eosin, erythrosin, rose of Bengal, cyanin, &c.

The most important work in the direction of ortho-chromatic photography has been carried out by Becquerel, Eder, and Vogel on the continent; Cary Lea in America, and by Abney, Waterhouse, and C. H. Bothamley in this country. The dyes may be employed in three ways, either by incorporating them with the sensitive emulsion in its preparation, dipping the sensitive plate when prepared in the solution of the dye, or coating the back of the plate with a varnish containing the specific dye to be used.

The amount of dye employed must be very small, as the effect is entirely destroyed by large quantities. When mixed with the emulsion it is generally found best to employ about 15–20 milligrams for every 500 c.c. of emulsion; but when the sensitive plate is dipped in the dye a solution of 1 part of dye in 20,000 of water is adopted.

The following curves, taken from Mr. Bothamley's excellent papers on this subject, show the increased sensitiveness produced by some of these dyes in the portion of the spectrum lying between A and E:—

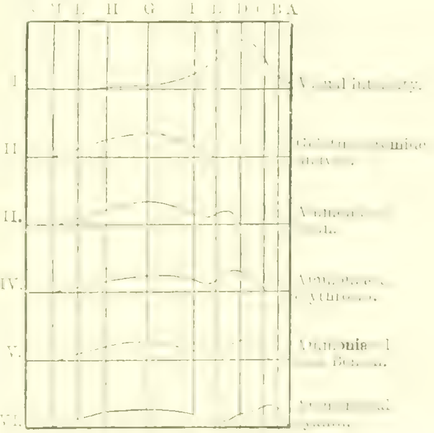

Fig. 5.

According to Mr. Bothamley's work, ammoniacal erythrosin seems to give the greatest sensitiveness for the yellow, and ammoniacal cyanin for the orange rays.

The chief use for plates so sensitised will be found in the copying of pictures or distinct patterns of different colours, where as much harmony as possible is required between the visual and photographic effect, but they will also prove useful in harmonising the contrasts which are sometimes to be found even in portraiture.

In preparing such plates an emulsion should be chosen containing little or no iodide. Having been coated and the emulsion dried, the plate is immersed for about two minutes in a solution of ammonia 1 part, water 100 parts; it is then placed without washing in the solution of the dye.

Dye (eosin, erythrosin, or rose of Bengal) . . .	1 part
Water	10,000 parts
Ammonia . . .	100 ,,

The solutions of the dyes insoluble in water may be made with alcohol, and carefully diluted to the proper amount. The method adopted by Mr. Ives, of Philadelphia, is very simple and efficacious. He soaks the plate for one minute in a solution of 1 grain erythrosin or cyanin, then allows to dry. When dry he washes with water and again dries; the plate is then ready for use.

These plates are extremely sensitive, and must be developed in dull ruby light.

Development of Dry Plates.

The development of dry plates produced either by collodion or gelatine emulsion is carried out either by an iron-salt—such as ferrous oxalate or ferrous citro-oxalate—or by what is termed 'alkaline development,' in which pyrogallic acid is the reducing agent, associated with the bromides of potassium or ammonium as retarders, and with ammonia, or the carbonates of potassium or sodium, as accelerators of the reducing action.

Development with ferrous oxalate.—This method is the simplest for ordinary dry plates, and may be employed for negatives on paper, and for enlargements on gelatino-bromide paper, but it does not permit correction of inaccurate exposure to such an extent as the pyro-developer. The ferrous oxalate developer may be prepared by adding 1 volume of a saturated ferrous sulphate solution to 4 volumes of a saturated solution of potassium oxalate. Such solutions are obtained by dissolving 4 ounces of neutral potassium oxalate and 6 ounces ferrous sulphate separately, each in 10 ounces of water. A solution of potassium bromide, containing 20 grs. bromide to the ounce of water, should also be made; of this, about 4 drops should be taken for every 2½ ounces of developer. The ferrous oxalate developer is applicable, not only to plates made with a gelatino-bromide emulsion, but may also be employed in the development of transparencies or positives made with a gelatino-chloride emulsion. It is, however, generally found better for this last-named emulsion to employ a ferrous-citro-oxalate, or ferrous citrate developer, with which, by varying the amount of the accelerator, graduated tones may be given to the transparency. The quantities given in the following table may be regarded as good standard quantities to be selected from :—

For Transparencies.

	—	*a*	*b*	*c*	*d*	*e*
I.	Potassium citrate .	200 grs.	—	—	—	—
	,, oxalate .	60 grs.	—	—	—	60 grs.
	,, bromide .	½ gr.	½ gr.	—	—	—
	Sodium chloride .	—	—	½ gr.	2 grs.	—
	Ammonium carbonate .	—	88 grs.	60 grs.	—	—
	,, chloride .	—	—	—	—	2½ grs.
	Magnesium carbonate .	—	—	—	76 grs.	—
	Citric acid . . .	—	120 grs.	180 grs.	120 grs.	—
	Water	1 oz.	1 oz.	1 oz.	1 oz.	1 oz.
II.	Ferrous sulphate .	80 grs.	—	—	140 grs.	15 grs.
	Sulphuric acid . .	1 mm.	same as for (*d*)	same as for (*d*)	1 mm.	—
	Citric acid . . .	—	—	—	—	7½ grs.
	Alum	—	gives warm tones	gives warmer tones	—	7½ grs.
	Water	1 oz.	—	—	1 oz.	1 oz.

To develop with the formulæ given in *a* and *e*, the solutions No. I. and II. are mixed in equal volumes. In *b*, *c*, and *d*, one part of No. II. is poured into three parts of No. I. To produce black tones in the transparency, the exposure should be short, and *a*, or even the ordinary ferrous oxalate developer, may be used. For warm tones a longer exposure is necessary, and solutions *b*, *c*, *d*, and *e*, may be employed. The solutions when mixed may be used for several plates in succession.

Development by ferrous oxalate or ferrous-citro-oxalate is simpler than with alkaline pyrogallate, but greater attention must be paid to the exposure, as there is less power of working up an under-exposed plate. This may be done, however, to some extent by adding, after development has proceeded some way, one or two minims of sodium hyposulphite solution from the fixing bath to the oxalate developer.

Alkaline development.—In this development it is to be remembered that the pyrogallic acid gives density, that the soluble bromide is supposed to act as a restrainer, and the ammonia or alkaline carbonate as an accelerator. The pyrogallic acid may be kept in the dry condition and added to the developer when required, but it is customary to keep all the substances as separate stock solutions, three in number. The stock solutions may be reduced to two in number, provided the pyrogallic acid and the alkaline accelerator are always kept separate, but in using two solutions the operator has not so much control over the retardation or acceleration of the development in cases of incorrect exposure. The amount of pyrogallic acid generally employed varies from between 1 grain to 5 grains per fluid ounce of developer, and full details of the correct quantities are almost universally given with the different makers' plates. The table at top of p. 213 gives some typical strengths of developers for different strengths of pyrogallic acid.

Developing solutions for gelatino-bromide plates.—The strengths of these solutions are given in grains and minims per one ounce of the developer, and are regulated for quantities of pyrogallic acid ranging from 1–5 grains.

The solutions should be kept separate; at least, the pyrogallic acid should not be mixed with the alkaline carbonates or the ammonia till required for use. II. may be termed the restrainer, and III. the accelerator. Solution *h* is particularly applicable to the development of paper negatives and stripping films. The different solutions may be kept separately in strong, or, as they are called, 'stock,' solutions, and diluted when required for use.

—		*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
I.	Pyrogallic acid	1·08 grs.	1·26 grs.	1·5 grs.	[illegible]	2 grs.	[illegible]	3·4 grs.	[illegible]
	Sodium sulphite	[illegible]	[illegible]	—	—	—	—	17 grs.	[illegible]
II.	Potassium bromide	—	—	—	—	—	[illegible]	—	—
	Ammonium bromide	1·08 gr.	1·26 gr.	1·5 [illegible]	2·4 grs.	2 grs.	—	—	—
III.	Ammonia	2·4 [illegible]	3 mm.	2·75 mm.	[illegible]	4 mm.	2·5 mm.	—	—
	Potassium carbonate	—	—	—	—	—	—	8·6 grs.	—
	Sodium carbonate	—	—	—	—	—	—	—	19 grs.

The manipulation required in dry plate development is very simple, as the operation is carried out in a dish. The plate, taken from the dark slide, is laid in the developing dish or tray face upwards, and if ferrous oxalate or citrate be used the proper quantity may at once be flowed over the plate, allowing the liquid to run gently from one end of the plate to the other. A gentle rocking motion may be given to the dish during development, so as to charge the liquid over the surface of the plate. The image gradually appears, the high lights gaining density first. Complete development may be recognised by a faint image appearing on the back of the negative, or looking through the negative at the red window or lamp, when the plate should show a very complete deposition of silver on the high lights. The knowledge of the exact extent for correct development can only be obtained by practice.

In the alkaline development it is sometimes customary to flood the plate first with the pyrogallic acid and bromide, and whilst this is in the dish to measure out the ammonia into the developing cup. The pyro. and bromide, with the quantity of water sufficient to cover the plate, are then poured into the cup, and after mixing with the ammonia returned to the developing dish. To commence development somewhat less than the full quantity of ammonia necessary should be used, and additional quantities added from time to time. The ammonia solution should never be added to the developer when in the dish, but should be placed in the cup and mixed with the developer in the manner just described.

The darkening of the film when the alkaline pyrogallic developer is used must not be allowed to go on so long as with the ferrous oxalate developer. In the former case the image is of a slightly yellow tinge, and consequently of a more non-actinic nature than that formed by the oxalate. It is not absolutely necessary that the pyro., bromide, and alkali should always be kept in three separate solutions; but this course is generally adopted to facilitate the retardation of the development when the plate is over-exposed, or its acceleration when under-exposed. If proper exposure has been given the image will appear in about one minute, and gradually gain in strength. When all the details are visible, and the development apparently stops, a few more drops of the accelerator may be poured into the developing cup, the developer mixed with it, and again flowed over the plate. This fresh addition of the alkali rapidly produces increase of density. When the development is deemed complete, wash thoroughly in a gentle stream of water from the rose-tap and place in the fixing bath, unless it be deemed necessary to soak the plate in the alum solution.

For the special development of dry plates for transparencies, or slides to be used in the lantern, the developers given in the following table will be found useful, and will give different tones to the transparencies:—

—		*a*	*b*	*c*	*d*
I.	Pyrogallic acid	20 grs.	20 grs.	20 grs.	—
	Potassium meta-bisulphite	60 grs.	—	—	—
	Ammonium bromide	20 grs.	—	30 grs.	—
	Ammonium sulphite	—	90 grs.	100 grs.	—
	Potassium bromide	—	10 grs.	—	1 [illegible]
	Potassium oxalate	—	—	—	2 ozs.
	Hydrochloric acid	—	20 mm.	—	—
	Water (distilled)	10 ozs.	10 ozs.	10 oz.	10 ozs.
II.	Liquor ammoniæ	$1\frac{1}{4}$ drms.		$1\frac{1}{4}$ drms.	
	Sodium carbonate	—	220 grs. ($\frac{1}{2}$ oz.)		
	Sodium sulphite	—	220 [illegible]		
	Ferrous sulphate	—			3 ozs.
	Sulphuric acid				6 mm.
	Water	10 ozs.	10 ozs.	10 ozs.	9 ozs.

Of *a*, *b* and *c* take equal parts just before development of I. and II. Of *d* take 6 parts of I. to 1 part of II.

Recently two other substances have been introduced as developing agents for dry plates, hydroquinone $C_6H_4(OH)_2$ and eikonogen (*v. supra*). Both these substances mixed with the proper proportions of alkali, potassium bromide, and sodium sulphite act as reducing agents, producing very clear negatives. In using these developers, the bromide and alkali may be employed as restrainer and accelerator precisely as already described in the alkaline development.

The following quantities of these substances will be found convenient for general use : –

—		a	b	c	d
I.	Hydroquinone	40 grs.	40 grs.	40 grs.	60 grs.
	Sodium sulphite	40 grs.	—	—	480 grs.
	Potassium meta-bisulphite	—	20 grs.	30 grs.	—
	Potassium bromide	—	—	5 grs.	10 grs.
	Citric acid	5 grs.	—	—	20 grs.
	Water	10 ozs.	10 ozs.	10 ozs.	10 ozs.
II.	Caustic potash	80 grs.	—	100 grs.	—
	Sodium sulphite	80 grs.	—	—	—
	Potassium carbonate	—	400 grs.	—	600 grs.
	Water	10 ozs.	10 ozs.	10 ozs.	10 ozs.
III.	Potassium bromide	12 grs.	—	—	—
	Water	½ oz.	—	—	—
IV.	Caustic potash	80 grs.	—	—	—
	Water	10 ozs.	—	—	—

For normal exposure equal parts of I. and II. should be taken; for over-exposure, less of No. II. to begin with. Solutions III. and IV. can be used for accelerating or restraining, as already described. Solution *d* is suitable for the development of lantern slides and transparencies.

Eikonogen is the sodium salt of amido-β-naphthol-sulphonic acid ($C_{10}H_5.NH_2.OH.SO_3Na$), and may be used in solutions of varying strengths, as found most convenient. The following quantities illustrate strong and weak developers with this substance:

Eikonogen	5 grms.	5 grms.
Sodium sulphite	20 grms.	45 grms.
Water	300 c.c.	500 c.c.
Potassium carbonate		60–75 grms.
Sodium carbonate (crystals)	15 grms.	
Water	100 c.c.	500 c.c.

Intensification and reduction of dry-plate negatives.—If proper exposure be given to the plate the process of development by the ferrous salt or by pyrogallic acid will always yield sufficient printing density. Both under- or over-exposure, however, will yield an image far too thin to give a vigorous and brilliant print. This deficiency may be remedied to a certain extent by the process of intensification; but it must be understood that the results, when such a process has to be employed, are never so brilliant as with a properly-exposed and properly-developed negative.

Several methods are in general use for the intensification of dry plates, one of the most usual being that in which the action is carried out by a mercury salt and ammonia. In dry-plate work the process of intensification is almost invariably carried out after fixing. For this purpose it is necessary that the last traces of sodium hyposulphite should be removed from the negative by thorough washing. Should it be necessary to take still further precautions for the removal of the last traces of hyposulphite, the negative should be soaked in a saturated solution of alum containing 3 grains of citric acid to the ounce of solution, or in a solution of hydrogen peroxide containing 1 drachm of 'Robins's hydrogen peroxide solution' to 5 ounces of water. The plate may be soaked in these from 10 to 30 minutes, and again washed before intensification.

To intensify, first soak the plate in water to thoroughly soften the film, then place in the following solution, preferably in a black vulcanite dish:

Mercury bichloride	200 grs.
Ammonium chloride	200 grs.
Water	10 ozs.

The plate rapidly undergoes a process of bleaching, and when the film is bleached throughout it is removed from the solution and thoroughly washed under the tap. The washing in this case must be most thorough. After this washing the plate is flooded with a solution of ammonia:

Ammonia, ·880	3¼ drms.
Water	10 ozs.

In this solution the plate rapidly assumes density, becoming changed first to a rich non-actinic brown, and finally to black, according to the length of time it has been left in the mercury bath.

Should only a slight degree of intensification be required, the ammonia solution may be replaced by a solution of sodium sulphite containing 1 ounce of sulphite to 10 ounces of water. The plate must be thoroughly washed before being placed in the sulphite solution.

Other intensifiers may be used, of which the the most useful will be found in the table on next page.

Solution *a* is applicable both to collodion and gelatine plates. To intensify with this solution, flood the plate with sufficient of No. I., then pouring off, add for every ounce of that solution 20 minims of No. II. In solution *b* the ingredients are dissolved in separate quantities of the water. The iodide solution is added to the mercury solution first, and the solution of hyposulphite then poured into the mixture formed. This intensifier has yielded good results in the hands of Mr. B. J. Edwards, who first introduced it.

In *c* the intensification is produced by the dark brown of the uranium salt deposited. In *d* the lead salt at first produced is white, and this is converted into black sulphide by the ammonium sulphide.

		a	b	c	d
I.	Pyrogallic acid	2 grs.		—	—
	Citric acid	2 grs.		—	—
	Mercury bichloride	—	60 grs.	—	—
	Potassium iodide	—	90 grs.	—	—
	Potassium ferricyanide	—	—	15 grs.	30 grs.
	Sodium hyposulphite	—	120 grs.	—	—
	Uranium nitrate	—	—	15 grs.	—
	Lead nitrate	—	—		20 grs.
	Water	2 ozs.	10 ozs.	4 ozs.	1 oz.
II.	Silver nitrate	20 grs.	—	—	—
	Ammonium sulphide		—	—	1 oz. (soln.)
	Water	1 oz.	—	—	10 ozs.

In all cases the plates should be well washed between the application of solutions I. and II. and after intensification; they may also be placed in the fixing bath again for a minute or two with advantage, and then finally washed.

Reducing negatives.—Should the negative after development and fixing appear too dense for printing purposes, one of the following courses of treatment will cause its reduction :—

(*a*) Immerse the soaked negative in a mixed solution of—

Potassio-ferric oxalate (saturated solution), 1 part.

Sodium hyposulphite solution (4 ozs. to 1 pint), 10 parts.

(*b*) Soak the plate in sodium hyposulphite solution (2 oz. to 1 pint) to which has been added potassium ferricyanide sufficient to give it a yellow colour.

(*c*) Soak the plate in a solution made by agitating 1 oz. good chloride of lime with 2½ ozs. of potassium carbonate in 12 ozs. of water. (The solution is best filtered through calico.)

Fixing the negative.—This operation is practically the same for dry plates as has already been described for wet plates, except that sodium hyposulphite is always employed and not potassium cyanide. The usual strength of the solution is 4 oz. of hyposulphite to 1 pint of water, but this may be varied according to the experience of the operator.

Transparencies.—When a positive picture is required for purposes of enlargement, or for showing on a screen to a large audience, it is found more convenient to employ an emulsion made of gelatine sensitised with silver chloride, alone or with a mixture of the silver chloride and bromide. The following quantities may be taken as giving good emulsions suitable for this purpose :—

	—	I.	II.
A.	Gelatine (Nelson No. 1.)	300 grs.	50 grs.
	Ammonium bromide	—	210 grs.
	Ammonium chloride	100 grs.	
	Sodium chloride	—	50 grs.
	Hydrochloric acid		5 min.
	Water	10 ozs.	10 ozs.
B.	Silver nitrate	240 grs.	400 grs.
C.	Hard emulsion gelatine	—	400 grs.

In No. 1 allow the gelatine to soften and swell in the water; then place all three vessels in a water bath at a temperature of 120°F. (49°C.). When the gelatine is melted add the silver solution to it, and then stir in the ammonium chloride solution. Allow the emulsion to ripen at that temperature for an hour, and pour out into a dish for setting. The details of washing the emulsion, coating, and drying the plates are the same as for the bromide emulsions already described.

As the film left by gelatino-chloride plates after development and fixing is extremely clear in the high lights, it is necessary for these plates to employ glass perfectly free from flaws or air bubbles.

Gelatino-chloride plates are less sensitive to light than the bromide plates, so that for contact transparencies from well-defined negatives an exposure of 10 to 20 seconds in diffused daylight, and from 2 to 3 minutes in gas-light about one foot from the flame, will be necessary.

These plates are best developed by ferrous oxalate, or by the mixture of ferrous oxalate and citrate previously mentioned, or by the hydrokinone developer. When rich warm tones are required, the oxalate may be mixed with a few minims of a 10 p.c. solution of sodium chloride, which also permits of more latitude in the exposure.

The chloride emulsion may also be used with paper as the substratum for the sensitive material.

Gelatino-bromide plates also yield good transparencies, but if they are used for this purpose a fairly strong pyro-developer should be taken and the development carried out quickly.

Transparencies are now commonly made by sensitive carbon tissue. A description of this method is given in the section on carbon printing, under the 'powder or dusting-on process.'

The formulæ useful in the development of transparencies are described under the development of gelatine plates.

Negatives on paper.—In the earliest form of negative—that introduced by Fox Talbot—the material employed as the substratum for the sensitive film was paper instead of glass. Although the employment of glass as a support to the sensitive film became generally adopted when the collodion process was perfected by Archer in 1852, the use of this material is gradually giving way at the present time to the employment of paper or hard gelatine films as the medium on which the sensitive emulsion may be spread. This reintroduction of paper as a basis for the sensitive film is due in a great measure to Mr. L. Warnerke, who in recent years has acted as a pioneer in the introduction of paper coated with emulsion, and in the design of apparatus necessary for the manipulation of such coated surfaces. Many other makers have followed on the same lines, and the employment of paper and other materials instead of glass as the substratum for the sensitive film is now rapidly gaining ground.

The details of coating the paper with the emulsion are nearly allied to those of coating the glass plate. The actual difference between the two methods consists in the special manner in which the sensitive films are arranged in the camera for exposure. This may be done in two ways. The sensitive paper may be cut into definite sizes the same as the glass plates, and then fixed by specially-constructed slips of thin wood in the ordinary dark slides exactly in the position that would be taken by the glass plate. Another method is to suspend the sensitive paper in a continuous roll in what is termed a roller slide, which takes the place of the dark slide containing the sensitive plate. In this arrangement the continuous slip of paper may be rolled off from one spool to another across the camera, a mechanical check or signal being given as soon as the length of paper corresponding to the width of the camera has passed over, thus placing a fresh surface in position before the lens. The process may be repeated till twenty-four or more portions of the continuous film have been exposed. The paper may then be removed from the dark slide for development, and another roll placed on the rollers in the slide. Many makers have now introduced slides and carriers for paper negatives in addition to Mr. Warnerke before alluded to.

The development of the paper negative may be carried out very much in the same way as a glass plate, but it is better to employ in the case of paper either the ferrous oxalate developer, or, if pyrogallic acid is used, a developer containing an alkaline carbonate with sulphite as accelerator, instead of free ammonia. Mr. Beach's formula or that given by the Eastman Company acts admirably. Development in the usual way by ammonia is by no means out of the question, but there is always the danger of a yellowish stain on the paper. If this method be employed, the paper should be soaked after fixing in an alum bath, with or without a little citric acid, as experience indicates, exactly like the glass plates. It will be found advantageous to soak the paper in water before development till all tendency to curl up has disappeared. Retardation or acceleration of the development may be done in the same manner as for glass plates. A marked difference between the negatives on paper and those on glass exists in the difficulty of determining during fixing when all the unaltered silver salt has been removed. Under these circumstances, it is best to allow the paper negative to remain twenty minutes in the fixing bath, when all the haloid salt will be removed.

Another difference is in the drying of the negative, which must be done on a glass or vulcanite support. The paper negatives, after thorough washing, are squeegeed face downwards to one of these supports, and placed in a moderately-warm place to dry. When dry the negative may be removed from the support by raising one end, and firmly but gently stripping it from the support.

Some paper negatives may be printed from at once as soon as they have been stripped from the support; others require to be greased before printing, so as to render them transparent and to remove the appearance of grain in the paper. To effect this the negative is fastened face downwards on a flat surface, and oil vaseline rubbed into the back by a little pad or one of the fingers. When the vaseline has thoroughly penetrated the paper, the negative, after standing for about twenty hours, will appear perfectly transparent, and the grain of the paper will have entirely disappeared. The excess of vaseline may be removed by a cloth pad.

The oil vaseline may be prepared by melting 3 parts of ordinary vaseline, and pouring into it 1 part of heavy lubricating paraffin oil. The details of printing from a paper negative are the same as for an ordinary dry plate.

Stripping films.—These films, which have been introduced within the last few years, consist of a film of hard gelatine rendered sensitive to light by an emulsion, and which is of such toughness as to furnish gelatine negatives which may be printed from after development, and fixing without either glass or paper as a substratum. The stripping film consists of a film of insoluble sensitive gelatine emulsion attached to a paper support by means of a layer of soluble gelatine. The exposure, development, fixing and washing these films are exactly the same as with the ordinary paper negatives, with this exception, that alum solution must not be used during the development, as it will render the layer of soluble gelatine insoluble.

After final washing, the film is laid face downwards on a clean glass plate which has previously been coated with a solution of india-rubber in benzol, and then with plain collodion. The film is pressed into contact with the prepared glass plate by means of a rubber squegee, then left between thick blotting-paper for half-an-hour under pressure. It is then placed in warm water, which dissolves the soluble gelatine layer and removes the paper, leaving a reversed negative on the glass. If it is deemed advisable, this may be printed from directly, retaining the glass plate as a substratum. The final removal of the negative from the glass may be accomplished by squeegeeing a clean gelatine skin into contact with it, allowing both films to dry, and then, gently raising one end, stripping the whole from the glass plate. The pellicle negative is then ready for printing from.

Gelatine films or plates can now be obtained made of the harder varieties of gelatine, upon which the sensitive emulsion is spread exactly as if the hard gelatine corresponded to the glass plate. These films are very light and portable, and by their use the difficulties connected with the manipulation of stripping films are removed.

Silver Printing.

For the multiplication of copies from a negative it is necessary that some light moderately-strong material, capable of being sensitised, should be employed. Hitherto paper coated with albumen has been the chief substance used. The albumenised paper is first treated with a solution of some soluble chloride, such as ammonium chloride, so that when brought in contact with a solution of silver nitrate its surface may be sensitised with the mixture of silver chloride and free silver nitrate. In the action of the light through the negative upon the sensitive paper a gradual darkening takes place during the decomposition of the chloride and albuminate of silver, and a copy or positive of the negative is produced, the lights and shades of the original object being truly represented. In ordinary silver printing the action of the light is allowed to proceed to such a length as to produce an image slightly darker than the print required, as the operations of toning and fixing have a tendency to weaken the colour of the print. Different organic substances might be and have been used instead of albumen, but that is the substance most generally employed.

As the colour resulting from the immediate action of a fixing agent on the silver compounds is a disagreeable red, the print undergoes the process of toning, which is effected by immersing it in a solution of gold, containing some substance capable of absorbing the chlorine derived from the decomposition of the silver subchloride produced by the action of the light. After sufficient tone of a brown or purple kind has been imparted to the print, the unacted-on silver compound is removed by sodium hyposulphite in the same way as with the wet plate.

To prepare the paper, coat with the following:

Albumen (white of egg) . . .	10 oz.
Ammonium chloride . . .	100 gr.
Spirits of wine	½ oz.
Water	3 oz.

Dissolve the chloride in the water and spirits of wine, then add the white of egg solution, with constant shaking for about half an hour, or, better still, break up the cellular membrane by mechanical stirring. Filter through a sponge or glass wool into a flat dish.

For plain salted paper the following quantities may be taken:

	a	b
Ammonium chloride .	30 gr.	50 gr.
Sodium chloride . .	15 gr.	
Sodium citrate . .	50 gr.	
Gelatine . . .	5 gr.	5 gr.
Distilled water . .	5 oz.	5 oz.

Dissolve the gelatine in the water, then add the other substances, and filter.

To coat the paper the sheet must be held carefully by two corners, gently bent back, and the centre of the convex side of the sheet lowered on to the solution in the dish. After two to three minutes raise, and again lower, to avoid air bubbles. Float on solution two or three minutes, then hang up to dry.

To sensitise the paper.—A silver solution, stronger than that used for sensitising the plate, must generally be employed. The following give varying strengths for different circumstances:

	a	b	c
Silver nitrate .	50 grs.	80 grs.	30 grs.
Water (distilled)	1 oz.	1 oz.	1 oz.

a may be used for ordinary cases, *b* where the negative is weak, and *c* where the lights and shades on the negative show great contrast. The strength of the bath becomes gradually lowered, and must be restored from time to time. Only strong negatives should be printed in direct sunlight; all other cases should be exposed only to diffused daylight or covered with tissue paper or coloured glass during printing.

Toning.—To obviate the red colour of the printed image, it is immersed in a neutral solution of gold containing certain metallic salts. The following are some selected toning baths:—

—	a	b	c	d	e
Gold chloride	1 gr.	1 gr.	1 gr.	1 gr.	1 gr.
Sodium acetate	30 grs.	—	—	—	—
Sodium phosphate	—	20 grs.	—	—	—
Sodium bicarbonate	—	—	30 grs.	—	—
Sodium biborate (borax) . . .	—	—	—	20 grs.	—
Sodium tungstate	—	—	—	—	20 grs.
Water	10 ozs.	10 ozs.	10 ozs.	10 ozs.	10 ozs.

a is a good bath for ordinary use, giving purple-brown tones, but should be made up twelve hours before use; *b*, *c*, and *d* can be used shortly after making, and give purple tones, but do not keep well; *e* gives fine purple-brown tones, and keeps fairly well in the dark. These solutions may also be made up in strong solutions by dissolving the tube of 15 grs. of gold in 15 ozs. of water, and adding the proper quantity of alkaline salt. To make the bath for immediate use mix 1 part of the stock solution with 10 ozs. of water.

The chemical reactions taking place in the process of toning do not appear to be complex in their nature, the tone being produced by a fine film of gold, reduced from a neutral solution of gold chloride ($AuCl_3$), or of the double salt ($NaAuCl_4$, $2H_2O$), upon the film on the print already containing the reduced products from the silver chloride and albuminate. To obtain the best results the gold solution must be neutral, and for this purpose it is mixed with certain salts, as the acetate, phosphate, biborate, and tungstate of sodium; bleaching powder, chalk, &c. The presence of reducing agents other than those formed by the reduction of the silver chloride and albuminate hinder the reduction of the gold; therefore the old plan of mixing the toning with the fixing bath should be avoided.

[illegible]—This is done by immersing the print, after toning, in a solution of sodium hyposulphite, 4 ozs. in 20 ozs. of water. This strength is suitable for prints from strong negatives, but where the print is weak the fixing bath may be reduced to 3 or 2 ozs. of hyposulphite to the pint of water. Before fixing, the prints should be immersed in water containing a small quantity of sodium carbonate for ten minutes, and then placed face downwards in the fixing bath. Their brilliancy will at first diminish, but will to a certain extent be restored when they are finally fixed and dried. The prints should remain in the fixing bath from 10 to 15 minutes, being gently moved about to prevent them sticking together. The prints must be washed after fixing for at least 24 hours in different changes of water.

In silver printing the toning bath should be neutral or slightly alkaline, and not below 60°F. The prints must be printed rather darker than finally required, and toned to a chestnut brown or purple.

Rapid printing with gelatino-bromide paper. From what has already been said with regard to paper negatives, it will be at once obvious that such coated paper may also be employed for direct contact printing. The arrangement in this case is the same as for silver printing, the gelatino-bromide paper replacing the silver paper under the negative. The exposure, however, is done in gaslight, and must be very short—from 5 to 20 seconds, 18 inches from the gas burner—and the print, not being visible after printing, must be developed as in the case of the silver paper.

The development of the picture is effected by ferrous oxalate or alkaline pyrogallate, and the fixing by the ordinary sodium hyposulphite.

The tone of these prints is distinctly neutral, and somewhat like platinum prints. The print may be obtained dull by allowing it to dry on blotting paper after final washing, with the sensitised side upwards, or it may be obtained with a glossy appearance by being squeegeed, face downwards, on a glass or ferrotype plate and allowed to dry in that position. When dry, it may be stripped from off the plate.

Printing with gelatino-chloride paper.—Printing on paper covered with a gelatino-chloride emulsion has recently much replaced albumenised paper. The details, so far as the printing is concerned, are similar to those of ordinary printing, except that it prints with considerably greater rapidity. The printing, like that with albumenised paper, should be carried slightly further than the shade finally required, as the prints diminish in intensity during toning and fixing.

Prints in gelatino-chloride paper may be toned by the following:

Gold chloride	3 grs.
Ammonium sulphocyanide .	100 grs.
Sodium hyposulphite . .	5 grs.
Water	10 ozs.

The gold is dissolved in the water separately from the salts, and the two solutions mixed immediately before use. The precipitate at first formed re-dissolves almost immediately. The toning must be carried further than in ordinary printing, and the prints may be fixed with hyposulphite directly after toning, without any intermediate soaking in water.

PRINTING IN PLATINUM.

Platinotype.—This method of printing was introduced by Mr. Willis, and has been patented by him. It may be divided into three distinct processes. In the first the paper is sensitised with a mixture of ferric oxalate and the platinum salt, and, after exposure, is developed with a hot solution of potassium oxalate. In the second there is no platinum salt on the paper, but it is coated with ferric oxalate containing a small quantity of mercuric chloride, and, after exposure, is developed by a cold solution of potassium oxalate with the platinum salt. The third process, introduced by Pizzigelli, differs from the first two in containing both the sensitive material and the developer on the paper during the operation of printing. It is, therefore, like silver printing, a printing-out process, where the image is carried to its full printing density during its exposure to the light, the print requiring no further development after exposure, but merely fixing.

In the first of these processes the action of the light produces the reduction of the ferric to ferrous oxalate, $Fe_2(C_2O_4)_3 = Fe_2(C_2O_4)_2 + 2CO_2$, leaving the potassium chloroplatinate unreduced in the film. On developing the partially-formed image, however, by warm potassium oxalate the ferrous oxalate becomes dissolved out of the film, and at the moment of its solution reduces the platinum salt, thus increasing the image by a deposit of metallic platinum,

$$3K_2PtCl_4 + 6(FeC_2O_4)$$
$$= 3Pt + 2Fe_2(C_2O_4)_3 + Fe_2Cl_6 + 6KCl.$$

Printing with hot developer.—In this case the paper is coated with a mixture of ferric oxalate and potassium platinous chloride, the probable change taking place during printing being the reduction of ferric to ferrous oxalate by the paper under the influence of the light. As there is an intimate mixture of the reduced iron salt with the platinum salt on the surface of the print, when this is floated on a warm solution of potassium oxalate the ferrous salt at once undergoes solution, but in passing into solution it reduces the platinum salt, and a deposit of metallic platinum is formed, varying with the amount of ferric oxalate reduced, which differs according to the amount of action of the light on the different parts of the plate. On the high lights the ferric oxalate remains unchanged, and therefore no reduction of platinum will take place on these during development.

The paper may be prepared by brushing it over with a saturated solution of ferric oxalate, containing 60 grs. of the platinum salt to the ounce of solution. It is necessary that the paper, after it is coated, should be kept absolutely dry; this is best effected by storing it in tin boxes with lumps of calcium chloride in a perforated chamber at one end of the tin. The amount of exposure requires perhaps greater experience than in silver printing, as allowance has to be made for the circumstance that the image on the paper before development is not sufficiently marked to guide the operator in determining the length of exposure without considerable experience. Proper exposure may be said to have been given when the shadows of the picture are distinctly seen of a drab colour.

For the further development of the image the print is floated face downward, or drawn over a hot saturated solution of potassium oxalate in the manner previously described for albumenising paper. A solution of the proper strength may be made by dissolving 2¾ ounces of neutral potassium oxalate in 10 ounces of distilled water, which should be used in a dish of enamelled iron and kept at a temperature of 170–180°F. When development is deemed complete, and the full detail of the picture is out, the print is transferred to a solution of hydrochloric acid, of a strength of 1 ounce hydrochloric acid to 60 ounces of water, in which it should remain ten minutes. The print must then be thoroughly washed in at least three changes of water. Should the prints be deemed over-exposed, the temperature of the developer may be lowered.

The prevailing tone of platinum prints is grey, but brown tones may be obtained by developing in a bath of hot potassium oxalate containing mercuric chloride.

Development with cold potassium oxalate.—In this modification of the process the paper is first coated with a saturated solution of ferric oxalate containing about 1 to 1¼ grains of mercuric chloride to the ounce of oxalate solution. After proper exposure as before described, the print is floated on a solution of potassium oxalate containing potassium platinous chloride. Considerable latitude may be permitted in the composition of this developer, but a solution containing 50 grains potassium oxalate to the ounce of water, with about 9 to 10 grains of the platinum salt, may be taken as a standard quantity to begin with. Warm tones are produced by lessening the quantity of potassium oxalate; cold or grey tones by increasing it.

The development by this method proceeds slowly, and may be stopped at any moment, great latitude being at the same time permitted. When the print is thoroughly soaked with the developer, it may be placed on a sheet of glass, or held in the hand, and the development watched. The intensity of the deeper shadows of the picture may also at this point be controlled by brushing over them some of the hydrochloric acid fixing bath, which checks the developing action, and allows of the denser parts of the picture being worked up.

[illegible]ment.—In this process, introduced by Pizzigelli, the paper is sensitised with a mixture of the platinum salt with sodio-ferric oxalate and sodium oxalate; under certain circumstances small quantities of potassium chlorate and mercuric chloride being also introduced. This method differs from the other two in the paper containing the sensitive salt and developer upon it during exposure, and the printing of the image being carried to its full extent. Under the influence of light and the moisture in the air, reduction of the platinum salt takes place in the printing-frame. The printing must be continued till the picture has the appearance finally required. In moist weather the printing will go on without difficulty; in very dry weather the increase of density apparently stops after a certain intensity has been reached; it will continue, however, to print, if the back of the paper be breathed upon or very gently steamed.

Fixing the prints.—This is best done by placing the prints in 1 vol. hydrochloric acid and 60 to 80 vols. water till the high lights appear perfectly white. They should then be washed in two or three changes of water. The tone given by platinum prints is especially applicable for copying buildings and machinery, but also yields most beautiful effects in portraiture when the proper lighting of the original negative has been attended to.

Toning silver prints with platinum.—If plain sized and salted paper be employed instead of albumenised paper, rich brown and black tones may be obtained by platinum. The resulting print has a dull or 'matt' surface, and the operations are very similar to those of ordinary silver printing.

The paper is first sized and salted simultaneously by one or other of the following solutions:

	(a)	(b)
Arrowroot . .	90 grs.	90 grs.
Ammonium chloride	80 ,,	60 ,,
Sodium carbonate .	—	120 ,,
Citric acid . .	—	30 ,,
Water . . .	10 ozs.	10 ozs.

The solution may either be spread over the paper, or, what is preferable, the paper floated on it as already described for coating albumenised paper.

After printing from the negative, toning may be carried out by the following solution. A stock solution of potassium chloroplatinite 30 grains to 1 ounce water, and

	(a)	(b)
Stock solution .	1 dram	1 dram
Water . .	2 oz.	8 oz.
Nitric acid .	1–2 mm.	2–3 mm.

(*a*) gives rich black tones, and for most purposes is too rapid in action; (*b*) allows of more gradation in the toning, and permits of the operations being better regulated. The prints are washed and fixed in a manner similar to ordinary silver printing.

In all silver printing processes the prints should be well washed, and the hyposulphite bath should be renewed as often as possible to prevent stains.

Printing with Iron Salts

Several processes have been brought forward in which the salts of iron may be employed instead of those of silver and platinum, thus rendering the cost of copying large plans or drawings much less expensive.

The reduction of the ferric salts by light was first utilised by Sir John Herschel, who employed the ammonio-citrate of iron as his sensitive material, developing the image with a solution of potassium ferricyanide, and the different methods now employed are more or less modifications of his original process.

By mixing the ferric salt and potassium ferricyanide together before coating the paper, the print may after exposure be developed by merely washing in water till the washings are colourless. For such a paper the following mixture will be found useful:

Potassium ferricyanide	600 grs.
Distilled water	5 ozs.
Ammonio-citrate of iron	600 grs.
Distilled water	5 ozs.

Dissolve the salts separately, then mix and keep the solution in the dark. The paper, after coating and drying, must be kept for a few days before use. When thoroughly exposed the print should show all details.

For increased rapidity it is better to use the method of development with the ferricyanide. Sensitise the paper with

Ferric chloride	1 oz.
Tartaric acid	1 ,,
Water	20 ozs.

Dry quickly, and expose under negative in direct sunlight for from three to five minutes. The image not being visible, experience must be relied on as in printing from gelatino-bromide paper.

The image is developed by floating the paper on a solution of 2 ounces potassium ferricyanide to 15 ounces of water. When the image is sufficiently developed, the print is well washed and finally dried. It is found advantageous in certain cases to add a small quantity of citric acid to the first wash water, as this tends to increase the brilliancy of the print.

A method for obtaining positive prints from positives may be carried out by sensitising the paper with the following solution:

Gum arabic	1½ oz. (troy)
Ferric chloride	1 ,,
Tartaric acid	½ ,,
Sodium chloride	½ ,,
Water	12 to 14 ,,

The paper, having been coated, dried, and exposed in the ordinary manner, may be developed by floating it on a solution of 1 ounce ferricyanide in 10 ounces of water. After development immerse in a cleansing solution of hydrochloric acid and water, wash thoroughly, and dry. These methods are extremely useful for copying large line drawings or diagrams, but may also be used for ordinary landscape and portrait prints.

A printing process, under the name of 'Kallitype,' in which iron salts are used has been recently introduced by Dr. W. W. J. Nicol. It consists in coating paper with ferric citrate, tartrate, or oxalate, or mixtures of these. The dried paper so coated is printed in a way similar to platinotype, and the development of the prints is carried out by solutions of potassium oxalate, or borax, mixed with silver nitrate of varying strengths.

They are then soaked in baths of an alkaline tartrate or citrate, rendered alkaline with ammonia, and finally washed with water.

DIAZOTYPE.

Under this heading may be classed two processes for printing in colours which may be shortly described in an article on photography. The one devised in Germany is termed *Feer-type* (from the inventor); the other *Primuline process*, introduced in England by Messrs. Green, Cross, & Bevan.

In the *Feer-type* the material is sensitised with a mixture of a diazo- compound with a phenol or amine in molecular proportions, dried in the dark and exposed behind a negative. The azo- colouring matter is produced in quantities proportional to the amount of light passing through the negative. After printing, the material is dipped in very dilute hydrochloric acid, and finally washed with water. The following table gives instances of some of the mixtures employed:—

—	I.	II.	III.
	Parts	Parts	Parts
Sodium toluenediazo-sulphonate	25	—	—
Sodium ditolyl-tetrazo-sulphonate	—	25	25
β-naphthol	25	—	—
Metaphenylene diamine	—	20	—
Resorcinol	—	—	12
Sodium hydrate	8	—	16
Water	1,000	1,000	1,000

Primuline process. If primuline be treated with nitrous acid (dil.), it forms diazo-primuline, which forms various colours by combination with different phenols and amines. If, therefore, a surface be dyed with primuline, converted into diazo-primuline, and exposed to light under a negative or pattern, and is then treated with a phenol or amine, an image is obtained, the colour of which is determined by the nature of the developer used.

The material may be dyed in a hot solution of primuline, washed and converted into the diazo- compound by a solution of 0·25 p.c. of acidified sodium nitrate. It is again washed, and allowed to dry in the dark. The exposure is regulated by exposing slips of the material during printing, and is known to be complete when the strip shows no colour on being touched with a drop of the developer to be used.

The development is carried out by an alkaline solution of a phenol or amine (0·25 p.c.). The following colours are given on developing with the following substances:

Alkaline solution of β-naphthol	Red.
,, ,, β-naphthol-di-sulphonic acid	Maroon.
,, ,, phenol	Yellow.
,, ,, resorcinol	Orange.
,, (slightly) pyrogallol	Brown.
α-naphthylamine hydrochloride	Purple.
Slightly acid solution of eikonogen	Blue.

CARBON PRINTING.

The processes considered under carbon printing may be described as those which yield a print, or transfer as it is usually termed, in some permanent colour or pigment. For convenience such processes may be arranged in three distinct classes. In the first division may be placed those processes the principle of which depends upon the fact that certain organic substances, such as gelatine, when mixed with an alkaline bichromate become insoluble in water after exposure to light. In the second may be classified those processes in which a tacky substance—such as gum, dextrine, or albumen—sensitised with a bichromate, is employed. In these cases when the plate is exposed to light the tackiness disappears, according to the intensity of the light and the extent of exposure, so that when an extremely fine powder is brushed over such plates it will adhere to the film on those parts shaded from the light by the dark portions of the negative. In the third division we have organic substances like bitumen, which by itself undergoes a change under the action of light, becoming insoluble in reagents like chloroform or benzene, in which it was freely soluble before exposure.

It will be readily seen that, if a surface such as is mentioned in the first instance be placed under a negative in a manner similar to that employed in silver printing, a graduated action of the light through the negative on the sensitive film will take place, producing an insolubility of the gelatine film, this depending on the different gradations of light and shade in the negative. The light passing freely through the shadows on the negative renders the gelatine film under them insoluble in water, whilst, there being little action through the deposits on the high lights, the portions under them will remain soluble, and can therefore be subsequently removed by proper treatment.

In actual practice it is the custom to mix with such sensitive films some colour or pigment in an extremely fine state of division, which, being retained on those portions of the film rendered insoluble by light, will represent, after the soluble portions have been removed, a copy in pigment of the original negative.

In a process belonging to the first division—namely, the bichromated gelatine—when the sensitive tissue is placed in warm water the soluble portions will be washed away and the insoluble will remain, thus forming a species of engraved sheet in which the high lights in nature are represented by the reliefs and *vice versâ*. In such processes there will be a reversal of the lights and shadows when copied by the print; thus in them a negative will produce a positive, and a positive a negative. But in the case of a process belonging to the second division, where a tacky substance is employed, a negative will produce a negative, and a positive a positive.

The basis of any pigment employed should be carbon, but the colour may be regulated to required tints by mixing it with suitable pigments, such as Indian red, Venetian red, Vandyke brown, umbers derived from iron oxides, or blue with indigo; in fact, with any colouring material which is of a distinctly permanent nature. The paper intended to support the sensitive material should be tough and smooth, and the gelatine employed should be of a medium quality, neither too soft nor too hard.

The carbon tissue, either fully sensitised or merely coated with the gelatine and pigment, may be purchased in the market, but in case of there being any necessity for its manufacture the following quantities may be employed; tissue, however, prepared on the small scale is not often very successful.

[illegible].—The paper may either be passed over the following mixture, the rate of transit regulating the thickness of the deposit:

Water	5	ozs.
Gelatine	600–750	grs.
Soap	75	,,
Sugar	105	,,
Colouring matter	20–40	,,

or a sufficient quantity of the mixture is poured on to a glass plate previously cleaned and moistened with oxgall. A sheet of the paper to be coated, slightly moistened, is then carefully laid upon the coated plate, and allowed to remain till the gelatine film dries. When this has taken place, the edge of the paper being gently raised, it may be removed from the glass plate with the film of gelatine adhering to the paper.

Sensitising the tissue.—For this purpose the tissue is floated on a solution of neutral potassium bichromate, formed by dissolving from 20–50 grains of bichromate to 1 oz. of water. These proportions may be raised to suit the negative to be copied and the season of the year. A weak bath is more suitable for warm weather, and a negative which may be filled with detail but is weak from over-exposure. A stronger bath should be employed when printing from a strong negative. The tissue should be dried, if possible, out of contact with any fumes arising from the combustion of gas or otherwise, and should be dried fairly rapidly.

Exposure. As no visible image can be seen on the tissue during printing, it is necessary to employ some kind of actinometer to regulate the time of exposure. Such an instrument may be formed by inclosing a slip of paper sensitised with a standard solution of silver in a small light-tight box. On exposing certain lengths of this paper different tints are obtained, corresponding to the different actinism of the light. Various forms of such an instrument have from time to time been devised, such as the actinometer employed by the Autotype Company, and the photometer designed by Mr. Woodbury. During the exposure of the carbon tissue the actinometer, with the exposed silver paper, is placed by the side of the printing frame. When the shade on the silver paper indicates that proper exposure has been given (a matter determined by previous experiment), the print may be removed and development proceeded with.

Development.—It will be most convenient, for the sake of clearness, to consider the process of development in two sections, commencing with the development of a pigmented gelatine film by means of a single transfer process, and to proceed afterwards to the method adopted when a plate prepared by a tacky substance has been used.

As will be readily understood, development must be effected in a weak light, and if much light is required it must be non-actinic. The process is carried out by the application of hot and cold water to the sensitive film when it has been placed on some suitable support, the final fixing or hardening of the gelatine film being [illegible].

For the development of a print at least three suitable dishes are necessary, a smooth board or sheet of zinc larger than the print, a squeegee for bringing the print and transferring material in intimate contact, and some sheets of blotting-paper.

To develop a print, place in one of the dishes with cold water a sheet of paper coated with plain gelatine (single transfer paper), and resting on the bottom of the dish gelatine surface upwards. Now place the print in the same dish, sensitised side downwards, and allow both to soak till perfectly limp; when both sheets have become quite flat allow them to float into contact, and then carefully withdraw them, still in contact, from the water; lay them on the flat board or sheet of zinc, and smooth steadily with the squeegee. The tissue and the transfer being now in contact, they may be laid between sheets of blotting paper for ten or fifteen minutes. After this the two sheets of paper are transferred to a second dish, containing water at a temperature of 38–44°C. (100–110°F.), when, after a few seconds, the pigment will be seen to gradually exude from between the print and the transfer paper. When this is seen, the upper sheet containing the carbon tissue may be gently separated at one corner from the transfer sheet, and completely stripped from it, leaving the tissue transferred to the lower or transfer paper. The original paper, which is now useless, may be discarded. The transfer paper now containing the image may be placed either in a dish or on the support, and the image developed by splashing the gelatine film with water or by pouring hot water over it from a jug. This gradually clears away the superfluous pigmented gelatine, leaving, after a minute or two, a permanent picture, repeating the detail and tone of the original negative. When development is deemed perfect the print is placed in a dish of cold water, and is finally put in an alum bath, which entirely removes the yellow tinge from the unaltered tissue and at the same time hardens the gelatine film.

Powder process.—This process is one of the oldest of the carbon processes, and is employed now almost entirely for producing prints upon a substratum of opal glass. The principle on which the process is carried out depends on the fact that when a tacky substance, like dried gum arabic, mixed with a bichromate, is dried and exposed to light, the 'tackiness,' as it is called, disappears in proportion to the intensity of the light. If, therefore, such a film be exposed under a negative, and after exposure be brushed or dusted over with a fine powder, this powder will be found to adhere to the tacky film in proportion to its tackiness, and a print will then be built up containing an image reversed as to left and right. It will be necessary, therefore, in order to obtain a true print, to first make a positive from a reversed negative of the original subject before printing. Many substances may be employed as a basis in this process, as may be seen from the following formulæ:—

	a	*b*	*c*	*d*
Ammonium bichromate . . .	4 drms.	—	150 mins.	—
Potassium bichromate	—	5 drms.	—	4 drms.
Dextrine	4 drms.	—	—	90 grs.
Grape sugar	4 drms.	3 drms.	—	4 drms.
Gum arabic	—	7 drms.	—	—
Honey	—	—	90 grs.	2 drms.
Albumen	—	—	90 mins.	3 drms.
Water	10 ozs.	10 ozs.	10 ozs.	10 ozs.

The introduction of albumen into the mixture necessitates additional care in mixing, as the froth must be allowed to disappear and the mixture then filtered as for albumenised paper. The albumen is an advantage afterwards, however, in fixing the image, as it is coagulated by the alcohol.

The coating of the substratum may be done in a manner similar to coating with collodion. If thought necessary, the surface may be previously coated with collodion, well washed, and allowed to drain. The bichromate mixture is then flowed over two or three times, allowing the excess to run back into the bottle, and the plate or substratum dried at a temperature of 65°C.

The exposure of the film may be effected in an ordinary printing frame, but must be done when the plate is perfectly dry and slightly warm. Although insensitive to light when wet, the plate becomes very sensitive when warm and dry; therefore, care is necessary. The length of exposure is best regulated by an actinometer, as the print cannot be examined during printing.

After printing, the film is exposed for a very short time to the air, but must not be allowed to absorb too much moisture; therefore, in damp weather it is advisable to warm gently before beginning development.

To develop, the film is gently brushed with plumbago in an extremely fine powder, the powder being kept in constant motion till the image is fully developed. Although there is a faint image on the film when taken from the printing frame, this is replaced by an image in powder during the development, which generally makes its appearance in a minute to a minute and a half. To increase the rate of development in an under-exposed print it is customary to blow gently on the film; care must be taken, however, that too much moisture from the breath does not pass over the surface, which would make the film too damp. When thoroughly developed, the surplus powder is gently brushed away.

The image is then fixed by placing the film in water to dissolve away the unacted-on bichromate and soluble gum, or it may be treated with a mixture of—

Methylated spirit	4 ozs.
Water	2 „
Sulphuric acid	$\frac{1}{2}$ „

which is flooded over the plate. The colour should be removed from the film in about five minutes, but if this does not take place a little more water may be added to the fixing solution. When fixed, the film must be soaked in methylated spirit and dried. It may then be coated with a good plain collodion, and finally with clear negative varnish.

Single transfers.—It will be observed that in the gelatine and bichromate process, which has been described, there is a certain disadvantage from the circumstance that in making the transfer from the negative a reversal of the image will have taken place from left to right, and *vice versâ*. There are many subjects in which such a reversal is of little or no consequence, but in making only a single transfer in a case where such a change of symmetry would be produced a reversed negative must be first taken and the transfer then made from it.

The methods generally adopted for taking such reversed negatives are by the reflection of the original negative from a mirror in front of the camera, or by printing a positive on glass and then printing from this a reversed negative on some sensitive film.

Double transfers.—There are, however, many subjects in which this reversal of the image is inadmissible, and for such subjects the double transfer process may be used. This process depends on the fact that when the exposed print is pressed in contact with a surface formed of wax or some similar substance the print will adhere to that surface as long as it is moist, but may be removed to another piece of paper on drying. Thus the print when wet may be laid on this temporary transfer surface and then developed, when, after development, if a second surface of paper be superimposed upon it, on drying the print will be found to strip away from the original support on which it was developed, and will therefore present on its new support no reversed image.

The supports for performing the transfer may be either rigid or flexible; in the former case, zinc or glass being used; in the latter, paper coated with insoluble gelatine, afterwards rendered waterproof with some form of lac. In employing sheet zinc as the support it should be gently and carefully rubbed with a solution of beeswax 90 grains, resin 180 grains, and oil of turpentine 5 ounces. The sheet of zinc having been placed face upwards in a dish, the exposed tissue is placed above it, and when thoroughly softened is firmly squeegeed to the zinc. Development, as described under the single transfer, is then proceeded with, and when completed the final support which is to retain the print is superimposed upon it, and the whole allowed to dry. When dry the final support is steadily stripped from the temporary support, when it comes away, bearing the proof upon it—now, of course, a copy in exact position. In employing zinc plates as the temporary support, it is necessary that the one side be ground or mulled with the greatest care, as the slightest scratches show on the print when transferred.

Flexible supports have been introduced by the Autotype Company, consisting of paper coated with gelatine rendered insoluble by alum. These supports must be waxed a short time before they are required for use, and should be cut slightly larger than the print transferred. Like the rigid supports, the flexible supports may be used over again, on being rubbed with wax before using for the first three or four transfers; after that it is not always necessary to rewax them.

Employment of bitumen.—Besides the gelatine film, sensitised with bichromate, there are other subtances sensitive to light which may be employed for the production of prints. One of these, bitumen, was referred to in the beginning of this article, and this substance in a pure condition was employed originally by Niepce. To obtain a form of bitumen most sensitive to light it should be exhausted first with ether, and the insoluble portion then dissolved in benzene. The ordinary liquid jet varnish does fairly well when diluted with an equal bulk of pure benzene. A properly-polished zinc plate is coated with a thin film of this varnish, the film being as evenly put on as possible, and when dry is exposed under a negative. It is then treated with a solvent, or a mixture of two solvents, as turpentine or benzene. The parts unacted on by light are rapidly dissolved, whilst the high lights remain untouched. As the turpentine dissolves bitumen slowly, and the benzene dissolves it quickly, by using them separately in the development it is possible to allow for considerable latitude in exposure. When final detail is visible, the plate is thoroughly rinsed with water and flooded in a dish with very dilute nitric acid kept moving on the plate. After about a minute's immersion, remove the plate and swill again with water, when the surface of the zinc plate, roughened by the acid, will allow the operator to see whether sufficient detail has been brought out. Should this not be the case, the plate must be again immersed in the solvent, and development completed. The image, on completion, may be exposed to light for a short time to still further harden the image, after which it is ready for etching in relief in the ordinary way. The images on such plates generally retain sufficient hardness to withstand by themselves excessive action of the acid in this last etching, without the necessity of alternately inking up the plates during the process, as is usually done in zincography.

Application of printing processes to lithography and mechanical printing.—From what has been said with regard to the carbon pigment processes, it will be seen that prints formed by such processes contain not only different gradations of tone, but also that such gradations are represented by varying reliefs in the gelatine film. The majority of so-called photo-mechanical processes at present employed are based on this circumstance, and the principles involved are utilised in many ways for the production of such reliefs on various surfaces, which may afterwards be covered with ink, and from which prints may be taken by the usual mechanical methods. Such methods may be broadly classified in two divisions—namely, such as produce a print from a surface where the lines and shadows are sunk, as in ordinary copper or steel engraving, and those which produce a relief or type block, like the ordinary wood engraving.

[illegible] which exist in the more mechanical details of these processes, it will be best to describe the chief points of importance connected with two methods of printing which form a connecting link between the photographic part of the subject and that of a more purely mechanical nature.

Woodburytype and Stannotype processes.—Taking advantage of the formation of gelatine reliefs just mentioned, Woodbury's process depends upon the production of a mould from the gelatine print in some hard material from which other copies may be mechanically taken. The first reliefs were obtained by electro-deposition of copper on the gelatine film, but, this yielding indifferent results, Woodbury introduced the method of stamping the gelatine film into a soft plate of metallic lead.

The following quantities may be employed in making the tissue :

Nelson's gelatine . . .	$3\frac{1}{2}$ ozs.
Sugar	1 ,,
Glycerine	100 grs.
Phenol	2 mins.
Indian ink	2 grs.
Ammonia, ·880 . . .	60 mins.
Ammonium bichromate	300 grs.
Water	12 ozs.

This is spread on a sheet of patent plate glass previously covered with a film of tough collodion. the details of coating and drying being similar to those of ordinary gelatine plates, with the exception that, as a deep relief is required, a very much thicker film of the sensitive mixture is required upon the plate. The films must be dried in a proper drying box with a current of air at about 27°C. (80·6°F.) circulating through it. When dry the films may be removed from the plates by the blade of a spatula, and carefully stored away from damp by inclosing them in tinfoil. They should be used within a day or two of coating. The sensitised tissue is now exposed under the desired negative, developed, and dried in the usual way. When dry it is placed on the smooth, soft metallic plate, and by means of an hydraulic press is pressed into the plate. The metallic mould of the gelatine plate is now placed in a special press, and a thick solution of gelatine, containing pigment or dye, is poured upon the plate. Strong paper of very even texture is now laid over the viscous gelatine, and the upper plate of the press brought down firmly on the sheet of paper. It is necessary that the top plate of the press, which is generally of strong glass, should fit absolutely on the top of the mould, so that all the superfluous gelatine may be pressed out. The print is then stripped from the mould when the gelatine has set, and hardened by being immersed in alum solution.

Stannotype process.—This process is a modification of the one just described, and was introduced by Mr. Woodbury himself to obviate the necessity of the hydraulic press in making the cast from the gelatine surface. It will be seen from the description of the Woodburytype that if the relief were produced from a positive instead of a negative, that relief might itself be used as a mould for the production of prints. This plan, however, is inadmissible, on account of the ink from its dampness at once destroying the sharpness of the gelatine mould. The Stannotype, therefore, is obtained by making a mould, not from a negative, but from a positive, which, to produce the proper sharpness in after-treatment, should be as good a one as possible. The mould for the Stannotype may be prepared in a manner similar to that described for the Woodburytype.

To coat the relief with tinfoil it must first be prepared by coating the relief edging with a thick solution of india-rubber in benzene or chloroform. After this is dry the surface of the relief is flooded with a thin solution of india-rubber in benzene (2 grains to the ounce). When set, a sheet of perfectly-smooth tinfoil, containing no pinholes, is spread over the surface of the relief and brought into intimate contact with it by passing the mould and the sheet of tinfoil between two rubber rollers, regulated to suit the thickness of the mould ; the flattening of the sheet of tinfoil being done as much as possible from the centre of the plates to the edges. Before printing on paper the mould should be gently oiled. The paper also should be prepared with a resinous surface by coating it with a solution of 1 part gum benzoin in 10 parts of alcohol, to which, after filtering, is added a warm solution of 1 part gelatine in 9 parts water. The gelatine ink having been poured into the mould under the printing press, the paper is superimposed upon it, the press lowered, and the ink allowed to set. When this has taken place, the press is opened and the impression stripped from the mould.

Collotype printing.—In this form of carbon printing, like those already mentioned, gelatine and bichromate are employed, but in the collotype plate, after exposure, it will be found, on damping with water, that the portions unaffected by light absorb water, whilst those affected, while repelling the action of the water, have acquired an affinity for fatty lithographic ink. It is thus possible to obtain from a *reversed* negative a print from nature in lithographic ink, the different gradations of tone being given by the amounts of ink taken up being proportional to the amounts of light acting on different portions of the plate.

To prepare the support for the collotype film, squares of glass, rather larger than the print required, are ground with very fine emery. This is best done by placing one of the plates on a strong support, dusting it with the finest sifted emery powder ; sprinkle with a little water, and then, superimposing a second plate, grind the two faces together till the emery powder works perfectly smoothly. Finally, wash with water and dry.

Before sensitising, the plates are coated with a substratum composed of either of the following :

(*a*)	Hard gelatine . . .	$\frac{1}{4}$ oz.
	Potassium bichromate .	$\frac{1}{4}$,,
	Water	12 ,,

The gelatine may be soaked in half the amount of water, melted, and the bichromate in the residual water then added. To this are added, at about 100°F., 6 ounces of albumen, and, when filtered, the melted solution is poured over the clean glass plate. When dried in the dark at the ordinary [illegible] be exposed for a short time to daylight till their colour changes from yellow to brown, when they must be washed in water till the washings are clear and allowed to dry. In this condition they will keep for some time.

(*b*) A second sub-stratum for collotype work may be obtained from a mixture of

Stale beer	5 ozs.
Syrup of sodium silicate . .	1 ,,

This should be mixed about 12 hours before use and filtered. The solution is flowed over the cleaned plate, which is then drained and placed in a level position in a drying box. When dry, the plates are removed, cooled, and washed under a tap for a short time. They are then dried spontaneously.

Before exposing, the plates receive the final coating, consisting of

Collotype gelatine . . .	2 ozs.
Potassium bichromate . .	½ ,,
Water	10 ,,
Ammonia	10 mm.

the solution being filtered through fine muslin.

To give the final coating, the plates should be raised to a temperature about 110 F., and, after receiving the film, should be laid in the drying cupboard in a horizontal position, and dried at about the same temperature. The plates are ready for exposure when dry and cold, but can be kept with safety for a day or two.

The collotype film is exposed behind a *reversed* negative in the usual manner. After exposure it is an advantage to lay the plate face downwards on some soft black substance, and expose the back of the film to diffused daylight from five to ten minutes.

[illegible] the plate in several changes of cold water till all trace of the bichromate has left the film. During this process the portions containing the high lights swell up, and the whole film, except where the deepest shadows are, assumes a fine grain or reticulation, and shows at the same time the image in slight relief. The plate is then soaked in a 1 p.c. solution of alum, again thoroughly washed, soaked in a dish of alcohol, and then allowed to dry. The plates may be used when finished, but it is best to allow them to remain a day before printing. It must also be kept in mind that, unless under very favourable conditions, only a limited number of inked prints can be obtained from one collotype plate, so that if many are required several plates should be made of the subject required.

To ink the collotype plate the usual lithographic ink may be used, thinned down by a little olive oil; or, if desired, two thicknesses of ink, with separate rollers, may be employed—the thick ink for the deep shadows and the thinner for the lighter tones. Before inking, the plate is slightly damped with a sheet of moist paper or sponged, and the ink vigorously rolled over it with a gelatine roller till all the details of the picture are complete. A sheet of paper is then placed over it, the press lowered, and a proof taken. The plate must be damped and inked between each impression. To obviate this re-damping it is sometimes customary to flood the plate, previously to inking it, with a solution of water and glycerine, with a little common salt.

[illegible] *graphy and photo-engraving.*—The operations in these two processes, so far as photography is concerned, are almost identical in principle, and differ only in details of manipulation; they may, therefore, in this article be dealt with in the [illegible] of the special details of printing and engraving is made under the different processes described.

The process is divided into three distinct operations—first, the preparation of a suitable print in greasy ink, which may be transferred to the stone or zinc plate; secondly, the laying down of this print on the stone, and thirdly, the production of prints from it by pressure.

The two first operations are those connected with photography, the last must be more fully studied in connection with practical lithography, engraving by acids, and printing.

The print or transfer paper necessary may be prepared in the manner already described for sensitive tissue, and is then exposed to light under the required negative, the length of exposure being judged by an actinometer or by the lines or shadows becoming of a dark-brown colour on a yellow ground.

The tissue is then laid on a flat surface of some kind, and covered with transfer ink; this may be done by inking the transfer directly with a gelatine roller, or first inking a stone or zinc plate, laying the transfer face downwards on the plate, and drawing through a press. The print is now laid face upwards in a bath of hot water at about 90°F., and after a short time is transferred, inked side upwards, to a glass plate or sheet of zinc, and treated with hot water at about 150°F., gently sponging in the manner already described in the development of carbon tissue. During this treatment the ink leaves all those parts of the print except those representing the lines or shadows, and the washing is continued till all the gelatine is removed from the surface which the ink has left. The transfer is then washed in several changes of cold water, and hung up to dry. It is well to leave the print for a day before transferring it to the stone. Before transferring it to the stone, the latter should be slightly warmed before a fire, or by pouring boiling water over it, and allowed to dry. It must then be set perfectly level in a printing-press such as is usually employed for lithographic printing.

To transfer to the stone block, the transfer paper is first laid face downwards on a clean sheet of thick paper and thoroughly damped upon the back by sponging or laying over it a damp sheet of paper. The damp transfer is next removed from the sheet of paper on which it was lying, and is laid gently face downwards on the surface of the prepared stone, care being taken not to disturb it after it has been laid down. A few sheets of paper are laid over it, and the whole passed through the press three or four times. When sufficient pressure has been given, the roller is removed, and the back of the transfer liberally moistened with warm water. After a short time, the transfer paper may be gently removed, when the gelatine image will be found to have been left on the stone.

The reason of this method will be readily understood. The greasy ink, having a certain attraction for the stone, remains with it, forming the lithographic picture, whilst the damp albumen on the paper holds the sheet in position, so preventing a slip of the material during the application of the pressure in the printing-press. The further printing from the stone is carried out in the same way as in ordinary lithographic printing.

Photo-zincography.—Before a zinc plate is ready to receive a photographic transfer, the surface should be finely grained by 'mulling' it with fine moulding sand. This graining should be continued till the surface of the plate is quite dull, and, if possible, should be done immediately before the transfer is to be placed upon it. For convenience in the subsequent manipulation in the printing-press, zinc plates are best screwed down to thick blocks of wood of a suitable height, which represent the lithographic stone. When the transfer has been successfully laid on the zinc plate in the way already described for stone, the next operation necessary is the etching of the plate, which is effected by a solution of which the following may be taken as a common instance:—

Decoction of nut galls .	15 ozs.
Gum water. . . .	5 „
Solution of phosphoric acid	3 drms.

The solution of phosphoric acid is made for this purpose by allowing sticks of phosphorus to stand half immersed in water in a bottle with a small opening to the air. The etching solution is brushed over the zinc plate, and allowed to act for a few seconds; it is then washed off, and the plate gummed in and dried. When dried, the surface of the plate is wiped with a cloth moistened in turpentine and olive oil, when the image disappears to a certain extent; it may now be covered with ink, which spreads over the whole surface of the plate.

When evenly black it is sprinkled with water and the inking by the roller continued; the image gradually becomes clear again, the ink being removed from all the parts not impressed with the transfer ink. Details relating to undercutting of lines in etching the plates and their means of prevention are given under the process dealing with the formation of type blocks.

Mechanical processes dependent on the principles already described for carbon printing.—From what has now been said with regard to the general methods of carbon printing, it will readily be seen of what advantage to ordinary printing the employment of such methods might become if adapted to the production of plates or blocks capable of being used with or without ordinary letterpress. In copying and transferring to blocks simple line subjects, no great difficulty has been experienced, but considerable skill and ingenuity has of late years been exercised in perfecting mechanical processes dealing with the reproduction of the natural half tones and transferring them to the printing-block. All such mechanical processes, however, so far as the photography is concerned, are based upon the carbon process, and differ only in the mechanical arrangements necessary for the final printing in ink, or the methods adopted for reproducing the natural half tones of the picture.

The blocks produced by these mechanical processes may for convenience be divided into four groups:—

(1) Those in which the lines or shadows are cut or etched under the surface, like an ordinary copperplate. Such are termed 'intaglio blocks.'

(2) Processes in which the various parts of the surface differ in their capacity for absorbing greasy ink, so that on inking the block or plate the different portions of the image are brought out in varying intensity, according as this power is greater or smaller for absorbing the ink.

(3) Those in which the portions of the plate designed to receive the ink are raised like an ordinary wood engraving, and where the half tones of the picture are produced by some stipple or grain previously given to the carbon print. This last form may be used for printing in the ordinary way with type, and the blocks receive generally the name of 'type-blocks.'

(4) Casting from swelled gelatine.

Methods of reproducing half tone by the use of grain or stipple.—The arrangements employed for the reproduction of the half tones represented in an ordinary negative are very various, and differ according to the method to be employed in the subsequent printing in ink. For the first class of prints, namely 'intaglio plates,' the graining required is very slight, so that in many cases it is sufficient to give to the plates just enough roughness to make it hold the ink. This result was originally produced in the early copper plates by the varying thickness of the bichromatised gelatine film after exposure. On being placed in the etching bath, the fluid acted more strongly when the gelatine film remained soluble, and less strongly when it had been rendered insoluble by the action of light. The varieties in the relief and the greater or less roughness on the plate produced by the etching gave quite enough stipple or grain for the attachment of the ink, reproducing to a certain extent the original half-tone effects. In the case of surface blocks the grain or stipple must be of a bolder character, and the relief must be greater than that of the intaglio plate.

The mechanical details necessary to produce the required grain may at the present time be arranged under one or other of the following methods: either the sensitive surface employed for the print contains some inert substance which is retained by the insoluble portions of the gelatine film, thus imparting to them a greater or less granular appearance according to the lights and shades of the original; or the half tones of the original negative are broken up in a purely mechanical way by covering the sensitive surface with a uniform network. This may be done by interposing a fine screen between the negative and the sensitive surface.

Of the first of these methods the simplest action of graining is found in the reticulation or marking which may be seen on wetting the bichromatised gelatine film itself, such reticulation being increased by the presence of a deliquescent salt. The character of the reticulation varies with the [illegible] the [illegible] posure to the light. In the [illegible] the [illegible]; where [illegible] acted it becomes entirely soluble and can be [illegible] away in development, [illegible] these cases no reticulation is found. In the graduated shadows, however, the reticulation will be slightest where the action of the light is slight, and will increase till it finally becomes merged in the solid shadows. A cast may be taken from such a film, and an electrotype from the cast, both of these retaining the reticulations of the gelatine film.

Another method, introduced by Mr. Woodbury and further developed by others, was the introduction of some granular material, like crushed glass or graphite, into the sensitive film from which an electrotype might be obtained retaining the original graining. The pounded graphite improves the conducting quality of the film, and renders the electrotyping easier.

FIG. 6. [illegible] GRAINS.

The devices resorted to in the production of grain by breaking up the lights and shades with a network are very various, and are in many cases trade secrets. Extreme care is necessary in the subsequent printing in ink, and probably the ultimate success of the copy is due as much to the skill of the mechanical printer as to the maker of the block. In all these mechanical manipulations, it must always be remembered that a considerable amount of hand skill may be, and generally is, expended on the blocks before they are printed from.

Fig. 6 shows instances of some of the artificial grains and stipples which may be used. These, having been carefully drawn on plates or sheets, may be photographed to the size most suitable to the grain or stipple of the negative required.

[illegible]

[illegible] Woodbury relief having already been fully described, it is only necessary here to indicate the further steps necessary to give a grain to such a copy. The relief having been taken in the ordinary way on sensitive gelatine which has the crushed glass or graphite incorporated with it, is then pressed into a sheet of lead or soft type metal, which receives the grained image. The lead being too soft to print from, it is coated with a film of copper of sufficient thickness to [illegible] hammer. [illegible] this copper film is again taken a second electrotype, from which the ink prints are struck off. It is probable that many of the photogravure prints are produced in a similar manner.

[illegible] the original etching process of Talbot, except that asphalt or powdered resin is introduced [illegible] A [illegible]-clean and polished copper plate is covered with a thin film of powder, which is caused to adhere by gently warming the plate and peppering the fine powder over it.

For refined work the plate may be coated with powder by placing it in a specially-constructed revolving box into which the powder has previously been put. A few revolutions are first given to the box, and it is then allowed to remain at rest for a few seconds to allow the heavier particles to settle. When sufficient time has elapsed, the door of the box is opened and the plate introduced face upwards on a proper support. The finer particles of powder are thus deposited and stick to the warm surface of the plate, the amount of powder deposited regulating the nature of the final grain. The plate is then gently warmed till its surface becomes glossy, when it is ready for use on cooling. A piece of ordinary carbon tissue with pigment in it, having been exposed under a reversed positive to form the print, is then squeezed down to the powdered copper plate, the temporary transfer is removed, and development proceeded with in the usual way.

The etching fluid consists of four solutions of ferric chloride of varying strengths, the strongest being first used, and the weaker ones afterwards. The back and edges of the copper plate should be varnished, and a rim of varnish or wax placed round the plate to hold the etching fluid. There being little pigment in the film, the action of the etching fluid may be easily watched through the film and so regulated. The etching process should be carried out at a temperature of 70° F. (21°C.).

Waterhouse process. A successful attempt has been made in this process to impart to the film what is termed a 'discriminating grain' that is to say, a grain where the dots will be larger in size where the shadows are greater, and correspondingly smaller as they pass into the highest lights.

A Woodbury relief is first developed on a thoroughly-cleaned and properly-polished copper plate, which, to prevent the adherence of the copper in the subsequent electrotyping, should be slightly silvered by washing with a solution of silver cyanide. The developed film when moist is sprinkled over with fine sand, emery, or glass powder previously coated with some greasy material such as wax, paraffin, or stearine, which prevents the particles permanently adhering to the gelatine. This coating of the sand is effected by heating a quantity of it in an iron pot with some melted wax, then removing the pot from the source of heat and stirring the mass till thoroughly cold.

As the gelatine film dries the particles are drawn into it, sinking deepest into the darkest parts, where there is most soft gelatine, less into the half tones, and not at all on the high lights where there is no gelatine. When the film has dried, the powder is brushed off with a moderately-stiff paint brush, when the surface will remain pitted with small holes largest in the shadows and diminishing gradually in the half tones. The plate is now ready for covering with blacklead and final electrotyping.

It is worthy of note, in connection with the question of 'discriminating grain,' that such an effect is produced also by the lateral action of the etching fluids on the sides of those portions of the gelatine films which happen to be protected on the top by some unacted-upon material.

A modification of the Waterhouse process has been introduced by Mr. Sawyer, in which he introduces powdered graphite into the gelatine film to obviate the necessity of coating with that material before electrotyping.

An extremely ingenious etching process has been devised by Obernetter, the principle of which depends upon the following reaction. A positive is first produced on a gelatine bromide film containing a large quantity of silver salt. The image having been developed and fixed, the reduced silver is first converted into chloride by the action of ferric chloride and chromic acid, and when wet is brought in contact with a copper plate. The chlorine apparently passes from the silver chloride to the copper, forming copper chloride, which, being soluble in water, can be washed away, so leaving an etched image on the copper plate.

Production of Half Tone for Photo-lithography.

Husband's papyrotint process.—In this process, which is a modification of Captain Abney's papyrotype for photolithography, the grain or reticulation necessary for the half tones is produced by some chemical change taking place between the ingredients mixed with the gelatine. The transfer paper may also in this process be used in contact with the negative, thus rendering the copy sharper than when interposed media are employed.

According to Major Husband, the paper is first coated with a mixture of:

Gelatine (Nelson's flake)	8 ozs.
Glycerine	1½ „
Sodium chloride	2 „
Water	50 „

It is dried for 10 or 12 hours at a temperature of 60°F. (15°C.), and, when required for use, is sensitised with:

Potassium bichromate	1 oz.
Sodium chloride	½ „
Potassium ferricyanide	100 grs.
Water	30 ozs.

The paper is then dried in the dark at 70°F. (21°C.), this latter part of the preparation being conducted in the dark room. After proper exposure, which should show the image of a light-brown colour on the yellow paper, the tissue is placed in cold water for about 10 to 15 minutes, and then spread on a flat glass and dried with blotting-paper. It is then gently sponged with a hard transfer ink, made by melting and mixing together:

White wax	½ oz.
Stearine	½ „
Resin	½ „

to which is added, when melted, 4 ozs. of chalk printing-ink, rendered of a creamy consistency with a little spirits of turpentine. On now inking with a roller, the ink adheres to the parts affected by the light.

The transfer is next placed in a bath of tannin and potassium bichromate for a few minutes, then removed, carefully dried between sheets of blotting-paper, and hung up for final drying. When thoroughly dry, the surface should be exposed to light for about two minutes.

Before placing on the stone in the lithographic press, the back of the transfer is moistened with a solution of oxalic acid, about 1 part to 100 parts of water, the excess removed by blotting-paper, and the print laid upon the stone. It is then pulled through the press twice in reversed directions, and the transfer taken from the stone without damping, when the ink will be found entirely transferred to the stone. The stone is then gummed up in the ordinary way as for lithographic printing.

In another method, devised by Asser, the transfer paper is coated with starch and bichromate. After exposure, it is necessary to heat the paper by placing it upon a previously-warmed block of stone or by ironing on the back. This heating causes the sensitive organic matter acted on by the light to absorb the lithographic ink. Before transferring to the stone, the back of the transfer is damped with weak nitric acid.

Production of Half Tones on Phototype Blocks.

The processes employed for the production of half tone effects—either in intaglio work or by collotype printing, as in photolithography—might be used for the production of type blocks, in so far as an image in suitable grain may be transferred to a zinc plate, and this etched in the usual manner. In actual practice, however, in the production of surface blocks it is now customary to employ the method mentioned at the commencement of the section—namely, that of copying a grain or network on the sensitive surface, or of introducing some granular material into that surface.

Meisenbach process.—This method developed from an earlier process, introduced by Messrs. Bullock & Swan, gives a favourable instance of how such blocks may be prepared. A grained screen or network is first made by copying the lines printed on paper from a specially-ruled copper plate. A transparency from the original negative having been taken, this is placed in contact with the [illegible], the [illegible] in contact, and a [illegible] by the [illegible]. From the negative so obtained a print may be taken on a zinc [illegible] or on paper coated with sensitive tissue; in this latter case, the print is afterwards transferred in the usual way [illegible]. The zinc plate after development is inked up as for ordinary lithography or zincography, and etched in the usual manner. For the engraving plate, it will be seen that it is necessary to reverse the negative to a positive and transfer the latter.

To render the breaking up of the lines in the shading more perfect, the stippled plate in contact with the negative may be shifted once or twice during the operation of printing.

[illegible] of relief blocks.—In this division of photo-mechanical printing considerable practice and experience are required, and it is only possible in this article to consider very shortly the different details of the process, which are, to a great extent, comparable with those of ordinary etching.

In actual practice several baths of the etching fluid, of different strengths, are used—generally about three, but sometimes more. For the different strengths employed, the special manuals dealing with these points must be consulted.

A finished transfer having been impressed on the surface of the polished zinc plate, it is first carefully inked up, so that the ink may take the lines and shading without any sign of spreading, and a thick marginal band of ink is spread round the edge of the plate. Powdered asphalt is now dusted over the plate, so as to saturate the inked surfaces with asphalt and increase the protecting material, and the excess is removed from the non-inked portions of the plate by dusting with a soft brush. The plate is now gently heated till the asphalt becomes incorporated with the ink, after which the operation of dusting with asphalt and incorporating it with the ink is repeated. The plate is now ready, and may be placed in the first etching bath.

Practice and experience alone can tell what length of time the plates should remain in the different etching baths, but one of the chief points to be attended to is the prevention of any undercutting of the raised lines by the etching fluid creeping under the portions protected on the top by the ink and asphalt. To obviate this the plates are removed from the baths at intervals, rinsed and dried, and treated in the following way: The plate is dusted with fine powdered resin, which sticks to the inked lines, and the excess of which may be blown off from the other parts of the plate. When the excess has been removed, the plate is gently heated till the resin just begins to flow and slightly widen the lines. It is then again dusted with asphalt powder, which incorporates itself with the resin, and on looking at the plate it will be seen that not only the tops, but the sides, of the raised lines have become coated with resin and asphalt, thus protecting the line from the biting-in and undercutting action of the acid. This process of covering with resin and asphalt powder is continued at intervals, according as the spaces between the lines become deeper and deeper.

The figure illustrates the different stages during the biting-in of the zinc plate.

During these several etching processes the back and sides of the plate must be protected by a coat of shellac varnish. To examine the condition of the plate during the different stages of etching, it may be cleaned by gently rubbing with turpentine and clearing off with dry sawdust. The ridges or markings which invariably occur between the different etching operations are generally smoothed away by an engraver's tool when the etching is considered to be finished. For full details of the precautions necessary, the manuals on etching must be consulted. In the final printing operations the zinc plate is strongly mounted on a piece of wood, and may then be placed in the printing press.

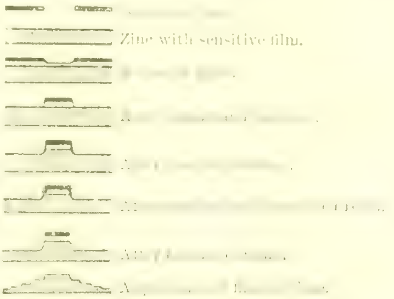

FIG. 7.

The description of the etching process has been given in connection with zinc, but for very fine work, especially for half-tone effects, copper plates should replace zinc.

The mechanical operations and details are virtually the same as for zinc, but the etching fluid is sometimes different. Two useful etching [illegible]:

(*a*) Perchloride of iron . .	1 oz.	
Water	20 [illegible]	
	I.	II.
(*b*) Hydrochloric acid .	5 ozs.	. 10 ozs.
Water . . .	95 ,,	. 70 ,,
Dissolve, and then add solution of		
Potassium chlorate	1 oz.	. 2 ozs.
Water . . .	50 ozs.	. 20 ,,

Nos. (*a*) and (*b*)I. give very soft copper etching.

[illegible] this and some kindred processes much resembles that of Woodbury, in that a relief being taken from the gelatine film it is used to stamp down the grain on a paper already possessing an even and marked grain. The highest portions of the relief crush down the grain, rendering the paper under them flat, whilst the lowest parts of the relief do not touch the paper at all. Between the two extremes there remains a gradation of tone, produced by the various amounts of flattening-out in the graining of the original paper. In this process, also, a plaster cast may be taken from a swelled gelatine relief, and on this cast a stipple may be impressed by means of an elastic stamp. The inked impression is then transferred, first to a sheet of indiarubber, and then to stone or zinc, when it is finally etched.

Swelled gelatine process.—In such a process the sensitive gelatine film, after exposure under the negative, is allowed to soak in water, thus forming a raised mould of those portions of the film representing the lights of the original. From this, a plaster cast being first taken, a wax mould is made from it, this mould being finally electrotyped.

The substratum for these plates is made of 4 ounces amber gelatine, soaked, and finally melted in 15 ounces of water; 1 ounce of sugar and 10 to 20 drops of a saturated solution of chrome alum are added, and the whole filtered through muslin. The cleaned plates are first coated with plain enamel collodion, and then with the gelatine solution, placed on a level slab to set, and then on a rack in a current of dry air.

To sensitise the dried plate it is dipped in a solution of potassium bichromate 1 ounce, water 15 ounces, and methylated spirit 5 ounces. The plate should remain in this solution three to four minutes, and is then dried in the dark room. After proper exposure the plate is soaked in a bath of cold water till the portions representing the original whites have swollen. Care must be taken that the soaking is not carried too far, as it renders the edges of the raised portions soft and round. When sufficiently soaked it is removed from the water, carefully dried, and finally coated with the plaster mould.

The plaster should be thoroughly liquid, and when first poured on should be gently rubbed into the film, so as to avoid air bubbles between the cast and the film. When the cast, which should be about half an inch thick, is set and hardened, it is turned over, and the original plate gently removed from the cast.

To make the wax mould the cast must first be thoroughly and evenly soaked in water; it is then removed from the water, and the melted wax, mixed with the finest blacklead, is poured over it. When this is thoroughly set, it is gently removed, touched up, and trimmed, and from it is taken an electrotype in the usual way.

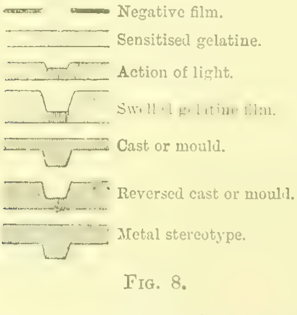

FIG. 8.

The figure represents the changes taking place in sections of the different materials during the process of casting, &c., from the original sensitive gelatine film.

It will be observed from this figure that in casting or moulding from the swelled gelatine the final stereotype obtained will have a slight roundness of the line. This is no disadvantage if the final printing in ink be carried out carefully, as by regulating the pressure in the printing press thicker or thinner lines may be obtained at will, thus giving a discriminating character to the picture.

Should, however, a sharper line be required, the unhardened portion of the gelatine may be entirely washed away from the hardened parts, leaving a raised portion as indicated in fig. 9.

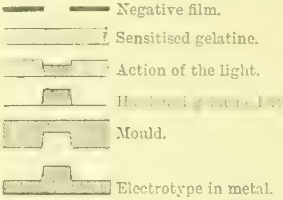

FIG. 9.

From this a wax mould, and finally an electrotype, may be taken.

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J. M. T.

PHOTOLITHOGRAPHY [illegible]

PHOTOPHONE *v.* Selenium.

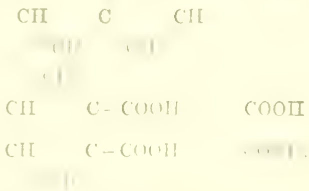
PHOTOSANTONIC ACID *v.* Santonica.

PHOTOZINCOGRAPHY *v.* Photography.

PHTHALEIN DYES *v.* Triphenylmethane colouring matters.

PHTHALIC ACID. The three dicarboxy-acids of benzene are frequently classed together as the *phthalic acids.* Of these the only one of technical importance is *o-phthalic acid*, $C_6H_4(COOH)_2$ (1, 2), and this is the compound which is always understood when the name *phthalic acid* is used without further qualification, the meta- compound being distinguished as *isophthalic acid*, and the para- as *terephthalic acid*.

o-Phthalic acid $C_6H_4(COOH)_2$ (1, 2). First obtained by Laurent, in 1836, by the oxidation of naphthalene (A. Ch. 61, 113). It is formed by the oxidation of benzene ortho-di-substitution-derivatives containing the group C_6H_4 attached to two hydrocarbon side-chains or to a closed hydrocarbon chain. Thus in the case of naphthalene the reaction may be represented as follows:



The oxidising agents employed are dilute nitric acid or an alkaline solution of potassium permanganate, or possibly chromic acid (*v. infra*).

The following are some of the compounds which yield phthalic acid on oxidation: naphthalene, naphthalene tetrachloride $C_{10}H_8Cl_4$, dinitronaphthol, alizarin, and purpurin with nitric acid; *o*-xylene and *o*-toluic acid with nitric acid or permanganate; phenanthraquinone, diphenic acid, and diphenyleneketone with permanganate. Benzene itself gives phthalic acid when oxidised with manganese dioxide and strong sulphuric acid in the cold (Carius, A. 148, 60), the explanation being that a portion of the benzene is first oxidised to formic acid, the latter substance being then oxidised simultaneously with a further quantity of benzene:

$$C_6H_6 + 2H.CO_2H + O_2 = C_6H_4(COOH)_2 + 2H_2O.$$

On a large scale phthalic acid may be obtained by the oxidation of naphthalene tetrachloride. The latter compound is prepared by adding a mixture of 1 part of naphthalene and 2 parts of potassium chlorate to 10 parts of crude hydrochloric acid (Häussermann, J. 1877, 763, 1,158). The product is washed first with water and afterwards with light petroleum. The naphthalene tetrachloride is then oxidised by boiling it with 10 parts of nitric acid (sp.gr. 1·45), which is gradually added during the process. The nitric acid is then evaporated off and the residue distilled, when phthalic anhydride passes over, and may be further purified by sublimation. It is the anhydride which is required by the manufacturer; phthalic acid, as such, is not manufactured, but may be obtained from the anhydride by boiling the latter with an alkali, so as to convert it into a phthalate, and then precipitating the phthalic acid with hydrochloric acid.

The naphthalene tetrachloride employed in the above process may also be obtained by passing chlorine into melted naphthalene, but the method is less advantageous than the foregoing (E. Fischer, B. 11, 738).

According to Lüddens (Chemiker-Zeitung, 1891, 585), phthalic acid is now manufactured by the oxidation of naphthalene itself with a mixture of potassium chromate (not bichromate) and sulphuric acid. The method of applying the reaction has not been made public.

Fuchs (Chemiker-Zeitung, 735), referring to the foregoing statement by Lüddens, doubts whether phthalic acid has ever been manufactured in this way. The method certainly is, as Lüddens himself admits, entirely opposed to the prevailing belief of chemists that ortho- compounds are destroyed by oxidation with chromic acid.

Friedländer, however, says (Fortschritte d. Theerfarbenfabrikation, 317): 'Latterly phthalic acid appears to have been prepared by direct oxidation of sulphonic acids of naphthalene, or by the action of nitric acid or chromic mixture on naphthol, points on which, however, further details are not forthcoming.'

Schultz (Chemie des Steinkohlentheers, ed. ii. 1, 762) also mentions chromic acid as an agent which may be substituted for nitric acid in the oxidation of naphthalene tetrachloride and dinitronaphthol in the preparation of phthalic acid.

Phthalic acid forms rhombic crystals. Whole crystals melt at 214°, powdered substance at 203°; in melting it decomposes into anhydride and water. 100 parts of water dissolve at 14° 0·54 part, at 99° 18 parts (Graebe, A. 238, 321). Readily soluble in alcohol, sparingly soluble in ether, insoluble in chloroform (separation from benzoic acid). Slightly volatile with steam. Heated with excess of lime it yields benzene and calcium carbonate; but when calcium phthalate is heated with half its molecular proportion of calcium hydrate to 330–350° it is converted into benzoate:

$$2C_6H_4<\begin{smallmatrix}COO\\COO\end{smallmatrix}>Ca + Ca(OH)_2$$
$$= (C_6H_5.COO)_2Ca + 2CaCO_3.$$

When calcium phthalate is heated alone it yields benzophenone, benzene, with small quantities of higher hydrocarbons, and a little anthraquinone. It forms crystallised salts, both acid and normal.

Phthalic anhydride $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O$. By distilling phthalic acid (Laurent), or by heating phthalic acid with acetyl chloride (Anschütz, B. 10, 326). Best purified by sublimation in a current of carbon dioxide. Long flexible needles melting at 128°. Boils at 284·5° (cor.). Scarcely soluble in cold, more readily in hot, water; gradually converted by boiling with water into phthalic acid. Readily soluble in alcohol and ether. Dissolves in alkalis, forming phthalates. With ammonia it yields phthalimide $C_6H_4<\begin{smallmatrix}C(NH)\\CO\text{——}\end{smallmatrix}>O$, and ammonium phthalamate $C_6H_4<\begin{smallmatrix}CONH_2\\COONH_4\end{smallmatrix}$. Phosphorus pentachloride converts it into phthalyl chloride $C_6H_4<\begin{smallmatrix}CCl_2\\CO\end{smallmatrix}>O$. By treatment with zinc-dust and acetic acid it yields phthalide $C_6H_4<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>O$, diphthalyl $C_{16}H_8O_4$, and other compounds. It readily condenses with phenols, forming the phthaleïns—a class of colouring-matters derived from triphenylmethane:

$$C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O + 2C_6H_5.OH$$
$$= C_6H_4<\begin{smallmatrix}C(C_6H_4.OH)_2\\CO\text{———}\end{smallmatrix}>O + H_2O.$$

Phthalic anhydride is employed in the manufacture of the phthaleïns. The commercial product should be free from phthalic acid, and should melt at 128°; it should give a clear solution with benzene, and volatilise without residue. F. R. J.

PHTHALIC ANHYDRIDE *v.* PHTHALIC ACID.

PHYSOSTIGMINE *v.* ORDEAL BEAN; also, VEGETO ALKALOIDS.

PHYCITE. A substance found by Lamy in *Protococcus vulgaris* (A. Ch. [3] 35, 138), and which he subsequently (A. Ch. [3] 51, 232) showed to be identical with erythrol (*q. v.*).

PICAMAR $C_{10}H_{14}O_3$ is easily obtained from wood tar; preferably from birch tar, which contains it in largest quantity. It is isolated by means of its potassium compound, which is purified by recrystallisation and decomposed by an acid; is a colourless, highly-refracting oil; b.p. 290° (cor.); and of sp.gr. 1·10228 at 15°. It has a bitter taste, savouring of peppermint, and a characteristic smoky smell. It is only slightly soluble in water, but freely soluble in alcohol and acetic acid. Its most characteristic reactions are the intense blue-green colouration which it gives with ferric chloride in alcoholic solution, and the insoluble compound it forms with the alkalis and alkaline earths. Heated with hydrochloric acid at 140° it is decomposed with formation of methyl chloride, and a crystalline product (m.p. 80°) identical in composition and properties with the substance similarly obtained by Hofmann (B. 11, 329) from dimethylpropylpyrogallol. This resolution of picamar may be expressed by the equation.

$$C_{10}H_{14}O_3 + HCl = C_9H_{12}O_3 + CH_3Cl.$$

The diaceto-derivative $C_{10}H_{12}(C_2H_3O)_2O_3$ is easily obtained by heating picamar (one part) with acetic anhydride (two parts) for two hours. Recrystallised from alcohol, it is obtained in long colourless needles (m.p. 83°). This is converted by the action of bromine into the dibromoderivative $C_{10}H_{10}Br_2(C_2H_3O)_2O_3$. The potassium compound of picamar $C_{10}H_{12}K_2O_3$ is easily obtained by the addition of alcoholic potash to the alcoholic solution of the substance. The above results indicate that picamar is the monomethyl derivative of a higher homologue of pyrogallol, probably propylpyrogallol, and may be represented therefore by the constitutional formula: $C_6H_2.C_3H_7.OMe(OH)_2$ (*v.* WOOD, DESTRUCTIVE DISTILLATION OF).

PICENE. Picene is contained in the least volatile portions of the residues from the rectification of petroleum. It is one of the least soluble constituents, and is best obtained by continual boiling with heavy coal-tar oils and a small quantity of strong sulphuric acid. Picene forms small colourless lamellæ, slightly affected by ordinary solvents, the best being aniline, toluene, and the heavy coal-tar oils. Fuming sulphuric acid dissolves it with emerald-green colouration; ordinary sulphuric acid acts in the same way. If in the latter case heat be gradually applied the colour of the solution changes from blue to greyish blue, and finally, at the boiling-point, to deep grey. It forms conjugated sulpho- acids, characterised by the beautiful blue-green fluorescence of their aqueous solutions. Picene melts at 335° to 337° C., and boils at 518° to 520° C. Its vapour density is 9·77, the formula $C_{22}H_{14}$ requiring 9·56. With picric acid it forms a red crystalline compound, easily decomposed by water and alcohol. It is an orange-red crystalline powder, which, on heating, is partly decomposed and partly volatilised in the form of thin needles. The latter melt at 190° C., are insoluble in water and sodium bisulphite, but easily soluble in cold sulphuric acid. When strongly heated with zinc-dust, picene is obtained, and at a lower temperature picene-oxide, a yellow body which resembles picene, melts at 290°, and has the formula $C_{22}H_{12}O$. Bibromopicene $C_{22}H_{12}Br_2$ is obtained by brominating a solution of picene in chloroform. It forms long white needles, melting at 294° to 296° C.

PICOLINE *v.* BONE OIL.

PICOLINIC ACID *v.* BONE OIL.

PICRIC ACID. Ordinary *trinitrophenol.*

$C_6H_2(NO_2)_3OH$ [$OH:NO_2:NO_2:NO_2 = 1:2:4:6$].

Picric acid was first obtained by Woulfe in 1771 by the action of strong nitric acid upon indigo; Welter (A. Ch. [1] 29, 301) subsequently prepared it by treating silk with nitric acid, and the product of these two reactions was subsequently more closely investigated by Liebig (Pogg. 13, 191; 14, 66; A. 9, 82), by Dumas (A. Ch. [1] 53, 178; [3] 2, 228), and by Laurent (A. Ch. [3] 3, 221), who showed it to be trinitrophenol, and identified it with the product of the action of nitric acid on phenol and dinitrophenol.

Preparation.—Picric acid can be prepared by the action of nitric acid on a large number of substances, as, for example, indigo (Woulfe), aloes (Schunck, A. 39, 7; 65, 234; *cf.* Marchand, J. pr. 44, 91), salicine (Piria, A. 56, 63), Botany Bay or acaroid resin—the resin of *Xanthorrhœa hastilis* (Stenhouse, Mem. Chem. Soc. 3, 10; Bolley, W. J. 1858, 460; Wittstein, D. P. J. 216, 272), gum benzoïn (Lea, Silliman's Amer. J. [2] 26, 381; Kopp, A. Ch. [3] 13, 233), silk, wool, leather, and other substances of complex composition. It is also formed by nitrating phenol (Laurent), ortho- and para-nitrophenol (Körner, Z. 1868, 323), 1:2:4- and 1:2:6-dinitrophenol (OH in 1) (Hübner, Schneider, and Henking, Z. 1871, 528), and phenolsulphonic acid (Schmitt and Glutz, B. 2, 52).

Picric acid was formerly manufactured from acaroid resin; Laurent's discovery of the fact that it forms the end product of the nitration of phenol led, however, to the adoption of this method for its production. At first impure phenol, b.p. 160–190°, was employed (Balard, W. J. 1862, 585), but this was soon replaced by the pure crystallised substance which is now very largely used.[1] To avoid the violent reaction which ensues on nitrating phenol, and to lessen the amount of resinous by-products, it is usual to sulphonate the phenol in the first instance, and then act on the resulting phenolsulphonic acid with nitric acid. According to Marzell (C. N. 37, 145), equal weights of pure crystallised phenol and sulphuric acid (sp.gr. = 1·843) are heated by steam at 100° in large iron vessels provided with mechanical stirrers, and the action is allowed to continue until a test specimen is completely soluble in water; strong nitric acid (4–5 mol. prop. to 1 mol. phenol) is then gradually added to the cooled product, which is kept well stirred until the reaction is complete. In some works the nitration is conducted in a second vessel, the phenolsulphonic acid being first diluted with twice the quantity of water, and then added gradually to the strong nitric acid contained in a stoneware vessel. In either case the picric acid is obtained as an oily, syrup-like mass, yielding large crystals on cooling; these are broken up, separated from the mother-liquor either in a filter press or centrifugal machine, washed once or twice with cold water, and then recrystallised from water containing about 1 p.c. of nitric acid, or $\frac{1}{10}$ p.c. of sulphuric acid. In this way much of the accompanying resinous matter is removed and the acid is further purified by conversion into sodium salt, insufficient soda-ley or sodium carbonate solution (Lea, Silliman's Amer. J. [2] 32, 182) being added in the first instance in order to bring about the separation of the remainder of the resinous matter. The filtered liquor is then rendered distinctly alkaline, whereby practically the whole of the sodium picrate is precipitated, owing to its insolubility in the alkaline liquid, and the precipitate is pressed, washed with cold water, and finally decomposed by adding an excess of sulphuric acid to its solution in boiling water—an excess of acid being employed, inasmuch as picric acid is practically insoluble in a solution of sodium bisulphate.

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[1] [illegible]

An increased yield of picric acid is said to be obtained by heating phenol with pyrosulphuric acid at 100–110°, and nitrating the resulting phenoltrisulphonic acid at 100° by the gradual addition of the calculated quantity of sodium nitrate (Eisenmann and Arche, Germ. pat. 51321 of May 8, 1889; Eng. pat. 4539 of 1889).

Properties.—Picric acid crystallises from water or alcohol in lustrous, bright-yellow scales or prisms, melts at 122·5°, and sublimes when cautiously heated but explodes if heated rapidly. It is sparingly soluble in cold, but more readily soluble in hot water, 1 part of the acid dissolving in 166 parts of water at 5°, 86 parts at 15°, 81 parts at 20°, 77 parts at 22·5°, 73 parts at 26°, and 26 parts at 77° (Marchand, J. pr. 44, 92). It dissolves in benzene to the extent of 8–10 p.c. at the ordinary temperature (Fritzsche, J. pr. 73, 282), and is also readily soluble in alcohol and ether. The acid has a very bitter taste, gives an acid reaction with litmus, and is poisonous. When boiled with bleaching powder solution it yields chloropicrin and chloranil (Stenhouse, A. 66, 241), and when heated with concentrated aqueous alkalis it is decomposed, with the production of hydrogen cyanide and ammonia (Post and Hübner, B. 5, 408).

Reactions.—A series of reduction products can be obtained by treating picric acid with various reducing agents—thus ferrous salts or alcoholic ammonium sulphide convert it into *dinitramidophenol* or *picramic acid* (Girard, C. R. 36, 421), formally used as a brown dye for silk and wool (Dollfus, D. P. J. 229, 108), aqueous ammonium sulphide reduces it to *diamidonitrophenol* (Griess, A. 154, 202), whilst tin and hydrochloric acid reduce it to *triamidophenol*, which is characterised by yielding a deep-blue colour when its aqueous solution is oxidised with ferric chloride (Roussin, W. J. 1861, 536).

Addition of potassium cyanide to a hot aqueous solution of the acid converts it into *picrocyanic* or *isopurpuric acid* (Hlasiwetz, A. 110, 290; Zulkowsky, W. J. 1868, 661; Kopp, B. 5, 644), formerly used in the form of ammonium or potassium salt, under the name *grenat soluble*, as a brown or reddish-brown dye for silk and wool.

Picric acid yields sparingly soluble or insoluble compounds with organic bases (*cf.* Smolka, M. 6, 917) and alkaloids, and, moreover, combines with many aromatic hydrocarbons, diphenyl being a noteworthy exception, forming molecular compounds which vary in their stability towards alcohol, and are readily decomposed by ammonia into their constituents (Fritzsche, *l.c.*; Berthelot, Bl. 7, 30; Nölting and v. Salis-Mayenfeld, B. 15, 1862).

Detection.—Picric acid is not volatile with steam, and can readily be detected by its bitter taste, the sparing solubility of its potassium salt, and its property of dyeing fibres and tissues of animal origin—*e.g.* silk, wool, the skin, &c.—yellow. Solutions of potassium cyanide (formation of isopurpuric acid) and potassium sulphide (formation of picramic acid) give, with picric acid in aqueous solution, red colourations which become yellow on great dilution (delicacy of test 1 part in 4000), but the most delicate test is the green crystalline precipitate produced by ammonio-sulphate of copper, which will detect 1 part in 5000 (Lea, Silliman's Amer. J. [2] 32, 182; *cf.* Christel, Fr. 23, 91).

Picric acid may be quantitatively estimated by precipitation with acridine, since acridine picrate is very sparingly soluble in cold water (Anschütz, B. 17, 439).

Adulterations.—Commercial picric acid sometimes contains impurities, which either are by-products—*e.g.* resin, oxalic acid, &c.—formed in its manufacture and insufficiently removed by washing, or are fraudulent additions. According to Winckler (W. J. 1858, 461), the following impurities may be recognised thus—(1) resin: dissolve 1 part of picric acid in 60 parts of boiling water, add $\frac{1}{2000}$ of the weight of sulphuric acid and filter. Any resin will be left behind on the filter paper. (2) Oxalic acid: examine the specimen microscopically, or dissolve 1 part in 100 parts of water, and estimate the amount by precipitating with ammonia and calcium chloride solution. (3) Nitre, or sodium sulphate: treat with alcohol to dissolve the picric acid present, and examine the saline residue by the ordinary method. (4) Sugar: neutralise with potassium carbonate, evaporate to dryness, and extract the sugar by repeated treatment with alcohol; then examine the alcoholic extract for sugar in the usual way.

Casthelaz (C. N. 15, 140) states that common salt and alum are sometimes used as adulterants in addition to the foregoing, and treats the specimen with benzene or ether, which extract the whole of the picric acid, but do not dissolve the oxalic acid and various salts which may be present.

Uses.—Picric acid has the property of dyeing animal fibres and tissues directly in an acid bath, but is not fixed by cotton or other vegetable fibres, unless previously mordanted with albumen or with a mixture of aluminium and magnesium acetates; hence it is sometimes used as a means of detecting cotton in undyed silk or woollen fabrics. Its tinctorial powers are great, and it produces on silk and wool a clear, bright yellow, which, compared with most other yellows, appears to have a greenish shade; but, owing to the colour being fast neither to light nor washing, picric acid is now but little used as a yellow dye, although it is frequently employed to produce compound colours with such dyes as benzaldehyde-green, methyl-violet, indigo-carmine, &c.

Salts.—Picric acid is a strong monobasic acid, and forms well characterised and for the most part sparingly-soluble salts, which are yellow or reddish-yellow in colour. *Ammonium picrate*, $C_6H_2(NO_2)_3ONH_4$, crystallises in bright-yellow scales or prisms, and is soluble in water but [illegible] soluble in alcohol; [illegible] [illegible] soluble in 10·11 [illegible], though almost insoluble in sodium carbonate solution; [illegible] crystallises in yellow prisms, and dissolves in 440·8 [illegible] (Frisch, J. pr. 100, 229), in 340·46 parts of water at [illegible] and 2[illegible]·17 [illegible] (Post and Mehrtens, B. 8, 1554), in 14 parts of boiling water, and in 1138 parts of 90 p.c. alcohol at [illegible] and 735·6 parts at 20° (Frisch): *lead picrate*, $(C_6H_2(NO_2)_3O)_2Pb+H_2O$, crystallises in brown [illegible] 0°, and 113·17 parts at 15° (Post and Mehrtens). The metallic picrates have been described by Marchand (J. pr. 23, 363; 32, 35), Lea (Silliman's Amer. J. [illegible]) [illegible] (Z. 1865, 189). See also Watts' Dictionary, 4, 403 (1866 ed.).

[illegible] said to explode on heating, but Berthelot has pointed out (C. R. 105, 1159) that this is only [illegible] small [illegible] suddenly heated, for when heated in any quantity the acid melts and gives off vapours which burn with a luminous flame without explosion; picric acid, moreover, does not under ordinary conditions explode by percussion. The picrates, on the other hand, are readily exploded by heating or percussion, and have been employed as explosives; lead picrate, for example, [illegible] sufficient oxygen for their complete combustion, [illegible] picrate with either nitre or potassium chlorate [illegible] picrate powder, for example, consisting of 54 p.c. ammonium picrate and 46 p.c. potassium nitrate (C. R. 69, 716). The volumes of gas liberated by the explosion of lead, strontium, barium, and potassium picrates respectively, and of mixtures of potassium picrate with 45 p.c. of nitre or 50 p.c. of potassium chlorate, have been measured by Roux and Sarrau (C. R. 77, 478; 79, 757), and the volume and composition of the gas, together with the composition of the residue produced by the explosion of potassium picrate under varying pressures, have been determined by Sarrau and Vieille (C. R. 93, 61). The temperature of explosion of lead, mercury, and iron picrates is 296°, that of potassium, ammonium, and magnesium picrates and of picric acid is 336° (Leygue and Champion, C. R. 73, 1478).

[illegible] solution of 58·3 parts of picric acid and 41·7 parts of nitric acid (sp.gr. = 1·5) explodes with great violence and without smoke when fired with a detonator (Sprengel, C. J. 1873, 800), and mixtures of analogous composition stiffened with asbestos have been patented by Punshon (Eng. pat., 2242 of 1880, 1132 of 1885) whilst Tschirner has patented an explosive consisting of 1 part picric acid, 1 part coal-tar, and 5 parts potassium chlorate (or potassium permanganate in about the same proportion), which is fired by percussion caps (Germ. pat. 15508 of Feb. 6, 188[illegible]) [illegible] have the double effect of decreasing the force of the explosion, and at the same time increasing the sensitiveness of picric acid to detonation. [illegible] sives invented, is said to consist solely of compressed picric acid. According to Turpin (Eng. pat. 15089 of 1885; Germ. pat. 38734 of Jan. 12, 1886; Zeit. für Chem. Ind. 1, 193) picric acid, when obtained in masses (1) by compression, (2) by admixture with gum arabic solution or with a suitable fat or oil, or (3) by admixture with 3-5 p.c. of collodion, can be exploded in closed vessels by 1-3 grms. of silver fulminate. The best results and the greatest insensitiveness are attained by fusion of the acid, since a mass of fused picric acid cannot be exploded in the open air by detonation with 3 grms. of silver fulminate introduced into the interior, although shells, torpedoes, &c., filled with liquid picric acid (fused at 130-145°), and cooled slowly, can be exploded by a charge of quick-burning gunpowder or a priming of picric acid powder detonated by 1·5 grms. of fulminate, the explosion being one of the most destructive known.

PICRIN [illegible]

PICROCROCIN [illegible]

PICROCYANIC ACID [illegible]

PICROGLYCION *v.* Dulcamara.

PICROPODOPHYLLIC ACID and **PICROPODOPHYLLIN** [illegible]

PICROSCLEROTIN *v.* Ergot of rye.

PICROTIN *v.* Picrotoxin.

PICROTOXIDE *v.* Picrotoxin.

PICROTOXIN. A poisonous crystalline compound, somewhat allied in its physiological action to strychnine, which occurs in 'Cocculus Indicus,' the small, berry-like fruit of *Anamirta paniculata* (Colebrooke, Bentl. a. T. 14), a climbing shrub of Eastern India and the Malayan islands. The drug does not find much favour in Western medicine, but is employed in India. Here it is better known for its power of stupefying fish and causing them to rise to the surface of the water in a state of intoxication, and as a reputed adulterant of malt liquors. On account of its poisonous properties, it sometimes becomes necessary to search for it in beer.

The small, black, ovoid fruit consists of a rough, tasteless pericarp, inclosing a reniform seed, which has an oily and bitter taste. The pericarp does not contain picrotoxin, but Pelletier and Couerbe isolated from it two crystalline compounds: *menispermine*, a base which melts at 120° and forms a crystalline sulphate, and *paramenispermine*, a neutral constituent which melts at 250°, together with a brown mass, *hypopicrotoxic acid*, which softens at 100° (A. Ch. [2] 54, 196). Half the weight of the seed is stearin. The *picrotoxin* exists to the extent of 0·4 to 1·0 p.c. It was discovered in 1812 by Boullay (J. Ph. [1] 4, 5). For *résumé* of work of Merck, Dutlos, Pelletier, and Couerbe, and others *v.* Gm. 14, 473.

To prepare picrotoxin, the method of Barth (J. pr. 91, 155; J. 1863, 586) and Barth and Kretschy (M. 1, 98) is usually followed. The seed is exhausted with boiling alcohol, the solution evaporated, and the fatty residue extracted with water. The aqueous solution is then treated with acetate of lead and filtered, and the filtrate, [illegible] sulphuretted hydrogen, is concentrated, when crystals of impure picrotoxin separate. These are purified by successive crystallisations from benzene and from water. Sometimes the seed is extracted with petroleum spirit in the place of alcohol (Marck, Ar. Ph. [3] 26, 269).

According to Barth and Kretschy (Sitz. B. 81, 7; B. 13, 1243), crude picrotoxin is a mixture of three compounds—picrotoxin, picrotin, and anamirtin—which are separated by fractional crystallisation from water and from benzene. This is, however, disputed by Paternò and Oglialoro (G. 10, 36; 11, 49; B. 14, 539), who regard the compounds named as decomposition products of a perfectly definite picrotoxin. Retaining the term picrotoxin for the original substance, these chemists propose picrotoxinin as a name for the picrotoxin of Barth and Kretschy. The decomposition of picrotoxin is thus explained: $C_{30}H_{34}O_{13}$ (picrotoxin) = $C_{15}H_{18}O_7$ (picrotin of B. a. K., previously called hydrate of picrotoxide by P. a. O.) + $C_{15}H_{16}O_6$ (picrotoxinin of P. a. O., pictrotoxin of B. a. K.). The conclusions of Paternò and Oglialoro are supported by the investigations of Schmidt and Löwenhardt (B. 14, 817) and Schmidt (A. 222, 313), while Barth and Kretschy have replied maintaining their original view (M. 5, 65).

Crude *picrotoxin*, $C_{30}H_{34}O_{13}$, the picrotoxin of Paternò and Oglialoro and of Schmidt, consists of brilliant rhombic prisms, which melt at 200–201° (B. a. K.), 199–200° (Sch.). It is intensely bitter and poisonous. It is very soluble in hot water, alcohol, or benzene, and sparingly so in ether or chloroform. Alkalis dissolve it readily, the solution being attended with complete decomposition, even in the cold. Picrotoxin is characterised by its reducing action on Fehling's solution, or ammonio-nitrate of silver, by the orange-red colour which it develops when warmed with concentrated sulphuric acid, and by a similar colour reaction which appears when it is mixed with nitre and concentrated sulphuric acid, and potassium hydroxide is added in excess (Langley, J. 1862, 628; *cf.* B. a. K., M. 2, 803). Picrotoxin forms compounds with many alkaloids (P. a. O.).

By the action of acetyl chloride in the cold picrotoxin is converted into *picrotoxid*, $C_{15}H_{16}O_6$, which melts at 310° (P. a. O.), 225° (Sch.), and is insoluble in most solvents (P. a. O., B. 10, 83, a. 1100), together with acetylpicrotin (Sch.). Picrotoxid, or isoprotoxid, and picrotin are also produced by the action of hydrochloric acid on picrotoxin in ethereal solution (P. a. O.). When a chloroformic solution of picrotoxin is allowed to stand in the cold, or a solution in water or benzene is heated, the picrotoxin gradually breaks up into picrotin and picrotoxinin (P. a. O., Sch.). *Picrotin* $C_{15}H_{18}O_7$ (P. a. O.), $C_{25}H_{30}O_{12}$ (B. a. K.), occurs in the seed in larger proportion than picrotoxin. It crystallises with varying amounts of water. Heated to 245° it darkens, and melts at 250–251°. It reduces Fehling's solution and ammonio-nitrate of silver. It possesses a bitter taste, but is not poisonous. Caustic potash decomposes it, but its solution in benzene or chloroform is unaffected by boiling or by hydrochloric acid. It forms crystalline acetyl and benzoyl derivatives (P. a. O., B. 12, 685; G. 11, 51; B. a. K., B. 13, 1243; Sch.). *Picrotoxinin*, $C_{15}H_{16}O_6$, H_2O, the 'picrotoxin' of Barth and Kretschy, is also formed in the reaction between acetyl chloride, hydrochloric acid, or bromine and picrotoxin (Schmidt). In the case of bromine a bromopicrotoxin $C_{15}H_{15}BrO_6$ results, which melts at 250–255° (P. a. O., B. 10, 1100; Sch.). Picrotoxinin crystallises in rhombic tables, which become anhydrous at 100° and melt at 200–201° (Sch.). It is bitter and exceedingly poisonous. It dissolves readily in hot water, benzene, alcohol, ether, and chloroform. Reduction and colour tests are given by picrotoxinin very similar to those obtained from picrotoxin. With benzoyl chloride it yields a crystalline benzoyl derivative, which melts at 237–238° (Sch.). *Anamirtin* $C_{18}H_{24}O_{16}$ occurs in small proportion in the seed, and collects in the aqueous mother-liquors in the preparation of picrotoxin. It is distinguished by its sparing solubility in chloroform and benzene. It is not bitter, is not poisonous, and does not reduce Fehling's solution or ammonio-nitrate of silver. Heated, it chars without melting at 280° (B. a. K.).

Cocculin $C_{19}H_{26}O_{10}$ is another constituent of the seed, discovered by Löwenhardt (A. 222, 353), and occurring only in small proportion. It is found in the alcoholic mother-liquors in the preparation of picrotoxin. It crystallises in needles, is difficultly soluble in hot, and insoluble in cold, water, alcohol, and ether, and does not give the colour reactions of picrotoxin.

For the detection of picrotoxin in beer the chemical reactions are not of much use. Extracts are prepared which are tested physiologically (*cf.* Langley, Am. S. [2] 34, 109; Schmidt, J. 1862, 629; Köhler, J. 1868, 796 a. 893; Blas, J. 1872, 936; Depaire, J. 1872, 946; Palm, Fr. 24, 556). A. S.

PICROTOXININ *v.* Picrotoxin.

PICRYL BROWN. A colouring matter belonging to the class of yellow, orange-yellow, and brown dyes introduced by Nölting and v. Salis-Mayenfeld, and obtained either by sulphonating nitro-derivatives of secondary and tertiary aromatic amines, or by the action of such compounds as dinitrochlorobenzene, trinitrochlorobenzene (picryl chloride), chlorotetranitronaphthalene, &c., on the sulphonic acids of aromatic amines (Germ. pat. 22268 of Aug. 31, 1882, expired Jan. 1887; W. J. 1883, 545). It is prepared (1) by sulphonating trinitrodiphenylamine (*cf.* Townshend, B. 7, 1249) with $2\frac{1}{2}$ times its weight of 40 p.c. anhydrosulphuric acid, or with 5 times its weight of sulphuric acid of 66°Bé., or (2) by boiling a concentrated aqueous solution of 3 parts sulphanilic acid, 3 parts picryl chloride, and $2\frac{1}{2}$ parts of sodium acetate. Picryl brown is soluble in water, and in an acid bath dyes silk and wool yellow.

PIGMENTS. A pigment is a powdered substance used as a colour. When mixed with a medium it constitutes a *paint*. The oldest examples of pigments are those discovered in the paintings of the Egyptians, who confined themselves to the use of red, yellow, green, blue, black, and white. To the Egyptians the Greeks owed their knowledge of painting, practised by them in its brightest period under Zeuxis and Apelles, 450–350 B.C., and in its decline under the Roman incursions.

Composition of Ancient Pigments.

[illegible]

Red. [illegible]

Yellow. [illegible]

Green. [illegible]

Blue. The 'Alexandria blue' (a silicate of [illegible] (ultramarine) (*v.* EGYPTIAN BLUE, vol. ii.).

[illegible] earths.

White. Chalk and plaster of Paris.

[illegible]

Red. [illegible]

Yellow. [illegible]

[illegible]

[illegible]

Purple. 'Grecian,' or 'Tyrian purple' (*v.* [illegible]).

[illegible]

Black. Carbonaceous substances.

White. Chalk.

Hence it will be seen that the colours which [illegible] substances. If, as probably was the case, vegetable colouring matters were employed, these have decayed, leaving no trace. Whatever their origin, however, the materials which were used by the ancients, and those used by artists up to quite recent times, were prepared by the artist himself or under his own supervision in his studio; but, as chemistry progressed, artificial [illegible] the present time our most important pigments are, almost without exception, artificial compounds made by the colour maker.

I. [illegible]

Colour. Generally each particle of a pig- [illegible] body which colours light by selective absorption; but, although the structural elements may be transparent, a body composed of such particles may be opaque. The effect of immersing a chromatically-coloured pigment in water is to add to it richness of colour with a loss of luminosity, because the effect of such immersion is to reduce the quantity of white light which is reflected from the surface of the particles. In oil this is the more evident, in the proportion that oil is more refractive than water. Consequently, much richer effects are produced by the use of oil as a medium than by the use of water; this greater richness being, moreover, permanent, since a dry film of oil remains refractive whilst no refraction remains in water-colour after drying. On the other hand, water-colour is specially effective for depicting atmospheric effects and for delicate colouring.

Transparency is the property which enables [illegible] the representation of shade.

Opacity, on the other hand, characterises pigments which are used for the expression of light.

Specific gravity is, of course, very variable in different pigments; but it may be taken that a distinct connection exists between high sp.gr. and great opacity, as *e.g.* red lead = 9·1; cadmium yellow = 4·8.

Working property depends upon the body and texture of pigments.

Body is often taken to mean opacity, but is more correctly defined as *tinging power*.

Crispness and setting-up are the qualities which retain a pigment in its place upon the canvas; when these qualities are absent, recourse is had to a gelatinous vehicle to confine them.

Drying power. The drying of oil is a chemical process whereby oxygen is absorbed from the atmosphere. This process may be facilitated or retarded by pigments. When the latter effect is produced, *driers* are made use of in addition. These are composed of the following substances: For light colours *sugar of lead*, *litharge*, and *sulphate of zinc*; for lakes—*japanners' gold size* and *boiled oil*; for darker colours—*manganese* and *verdigris*. Of these, the lead and copper compounds are destructive to the permanence of colours.

II. PERMANENCE.

Chemical change affecting pigments under the ordinary conditions of painting is effected in the following ways:—

1. By the action of light.
2. By the action of oxygen and moisture.
3. By the action of the medium.
4. By the mutual action of pigments.

1. *Action of light.* Light acts principally on pigments of organic origin and on the more unstable of the inorganic pigments. Molecules which are complex in structure, or which do not cohere by marked chemical affinity, are disintegrated by the vibrations of light; but, except to a slight extent and in the case of a limited number of colours, only when some moisture is present. *In vacuo* hardly any colour is acted upon by light. This action is more marked in water-colour than in oil.

2. *Action of the atmosphere.* This consists in the effects of oxygen and moisture present in pure air; and, added to these, the effects of sulphurous and sulphuric acids in polluted atmospheres; and it is mainly in relation to the ability of pigments to resist these agencies that their relative permanence must be considered.

In a 'Report to the Science and Art Department on the Action of Light on Water-Colours,' prepared in 1888 (Blue Book, C. 5453) by Dr. Russell, F.R.S., and Captain Abney, R.E., F.R.S., some interesting results are tabulated. From experiments, in which colours were 'subjected to conditions similar to those to which pictures are subjected, but to an exaggerated extent,' it was shown that in some cases the colour entirely disappeared. In the majority of cases only a part of the colour disappeared, the thinner washes fading out; but the following pigments remained unchanged: Indian red, Venetian red, burnt sienna, chrome yellow, lemon yellow, raw sienna, terre verte, chromium oxide, Prussian blue, cobalt blue, French blue, and ultramarine ash. The following table shows approximately the order of instability of the single colours under the conditions described, beginning with the most fugitive :—

1. Carmine
2. Crimson lake
3. Purple madder
4. Scarlet lake
5. Payne's grey
6. Naples yellow
7. Olive green
8. Indigo
9. Brown madder
10. Gamboge
11. Vandyck brown
12. Brown pink
13. Indian yellow
14. Cadmium yellow
15. Leitch's blue
16. Violet carmine
17. Purple carmine
18. Sepia
19. Aureolin
20. Rose madder
21. Permanent blue
22. Antwerp blue
23. Madder lake
24. Vermilion
25. Emerald green
26. Burnt umber
27. Yellow ochre
28. Indian red
29. Venetian red
30. Burnt sienna
31. Chrome yellow
32. Lemon yellow
33. Raw sienna
34. Terre verte
35. Chromium oxide
36. Prussian blue
37. Cobalt blue
38. French blue
39. Ultramarine ash

Show no change.

Out of 34 mixtures tried, only three remained unchanged from first to last; but six mixtures containing Prussian blue, although at first altered, returned more or less to their original colour on being placed in the dark for six weeks. This curious recuperative property of Prussian blue is frequently observed.

In another series of experiments on the same pigments, the atmosphere to which they were exposed was free from all moisture. Thirty-eight experiments were made with single colours ; but under this altered condition 22 instead of 13 were found to be permanent, these being principally those colours which in the first experiment were only slightly faded. In two cases (viz. brown madder and Prussian blue) the colour when exposed to ordinary air was not acted upon, whilst in dry air it was. The colours which were unchanged in dry air but were acted upon in ordinary air were madder lake, cadmium yellow, Naples yellow, emerald green, olive green, Payne's grey, sepia, and burnt umber.

In a third series of experiments the colours were exposed to air fully saturated with moisture. Out of 37 single colours only 10 withstood the action of light under this condition ; these were Indian red, Venetian red, burnt sienna, yellow ochre, raw sienna, emerald green, terre verte, chromium oxide, cobalt, and ultramarine ash. Twenty-nine mixtures were also tested in a similar way, of which only two remained unchanged, viz. raw sienna with Venetian red, and cobalt with Indian red.

To eliminate the effect of oxygen a further series of experiments was made, in which 36 single colours were exposed in an atmosphere of moist hydrogen gas. Of these no less than 22 remained unchanged; even carmine and crimson lake did not alter—neither did madder lake, Indian red, Venetian red, brown madder, burnt sienna, chrome yellow, yellow ochre, raw sienna, terre verte, chromium oxide, olive green, indigo, cobalt blue, French blue, ultramarine, permanent blue, Payne's grey, sepia, Vandyck brown, and burnt umber.

Another series of experiments was made, in which the air and moisture were, as far as possible, removed by an air-pump from glass tubes in which the coloured papers were hermetically sealed. In this series 39 single colours were exposed to light *in vacuo*, and hardly any colour was acted upon. Violet carmine and purple carmine slightly darkened; Prussian blue and purple madder and sepia slightly bleached, but in all cases the action was very feeble. Twenty-four experiments were made with mixed colours; hardly any change occurred in these, with the exception that vermilion blackened, and in mixtures containing Prussian blue the other colour became dominant.

In order to show at a glance the different effect produced by the action of the surrounding medium on colours exposed to light, the table on the following page is given. Under the heading of 'Altered' are included changes ranging from a very small destruction of colour to a very considerable one, and the classification is consequently only approximate.

Exposed to an arc light of an illuminating value of 2,000 candles at a distance of one foot for eighty-four hours, whether placed in a frame with glass in front or under the most favourable conditions for fading—viz., in sealed tube with moist air—those single colours selected as most easily acted upon underwent no change with the exception of crimson lake (bleached and more red) and carmine (bleached and more red); whilst, among mixtures, Prussian blue, yellow ochre and Vandyck brown, Prussian blue and raw and burnt sienna, and Prussian blue and burnt sienna, all became slightly browner; the other mixtures remaining unchanged. Exposed to gaslight, in a closed cupboard, for three weeks continuously, no colour experimented upon showed any material change. Crimson lake was slightly bleached, madder lake became a little redder, and Antwerp blue and Prussian blue a shade greener. Exposed to the rays of light falling respectively through red, green, and blue glass, the alteration was very slight in the case of the first two, and nearly, but not quite, approached the effect of white light in the case of the last-named, clearly showing that it is the blue end of the spectrum which is active in producing the fading of colours.

The conclusions drawn from these experiments are (*a*) that mineral colours are far more stable than vegetable colours ; (*b*) that the presence of moisture and oxygen is, in most cases, essential for a change to be effected even in the vegetable colours ; (*c*) that the effect of light on a mixture of colours which have no direct chemical action on one another is that the unstable colour disappears and leaves the stable colour practically unaltered ; (*d*) that the more refrangible rays produce by far the greatest change in a pigment, and that these, for equal illumination, predominate in light from the sky ; whilst they are less in sunlight and diffused cloud light, and are present in comparatively small proportion in the artificial lights usually employed in lighting a room or gallery. 'The experiments have also shown that about a century of exposure would have to be given to water-colour drawings in galleries, lighted as are those at South Kensington, before any very marked deterioration would be visible in them if painted with any but the more fugitive colours ; and that when the illumination is of the same quality

[illegible]

Moist air	Dried by [illegible]	[illegible]
No change Indian red. Venetian red. Burnt sienna. Yellow ochre. Raw sienna. Emerald green. Terre verte. Chromium oxide. Cobalt. Ultramarine ash.	*No change* Indian red. Venetian red. Rose madder. Madder lake. Aureolin. Chrome yellow. Cadmium yellow. Yellow ochre. Naples yellow. Raw sienna. Emerald green. Terre verte. Chromium oxide. Olive green. Cobalt. French blue. Ultramarine ash. Permanent blue. Payne's grey. Sepia. Burnt umber. Burnt sienna.	*No change* Indian red. Venetian red. Carmine. Crimson lake. Scarlet lake. Rose madder. Madder lake. Brown madder. Burnt sienna. Gamboge. Aureolin. Chrome yellow. Cadmium yellow. Yellow ochre. Lemon yellow. Naples yellow. Indian yellow. Emerald green. Terre verte. Chromium oxide. Olive green. Antwerp blue. Indigo. Cobalt. French blue. Ultramarine ash. Vandyck brown. Burnt umber. Brown pink.
Altered Scarlet lake. Vermilion (black). Rose madder. Madder lake. Brown madder. Gamboge (very slight). Aureolin. Cadmium yellow. Lemon yellow. Naples yellow. Indian yellow. Olive green (brown). Indigo. French blue. Permanent blue. Payne's grey. Violet carmine (brown). Purple carmine (brown). Purple madder. Sepia. Burnt umber (very slight). Brown pink. Vandyck brown.	*Altered* Carmine. Scarlet lake. Vermilion (black). Brown madder. Gamboge. Indian yellow. Antwerp blue. Prussian blue. Indigo. Leitch's blue. Violet carmine. Purple carmine. Purple madder. Vandyck brown (very slight). Brown pink.	*Altered* Raw sienna (slightly darkened). Prussian blue (slightly darkened). Violet carmine (darker). Purple carmine (darker). Purple madder (very slightly [illegible]). Sepia. Vermilion (blackened).
Destroyed Carmine. Crimson lake. Antwerp blue. Prussian blue.	*Destroyed* None.	*Destroyed* None.

as that of gaslight, or of the electric glow light rendered normally incandescent, and of the same intensity as that employed in those galleries, an exposure to be reckoned by thousands of years would have to be given to produce the same results.'—(Report.)

3. *Action of the medium.* Oil in drying absorbs oxygen in considerable quantity from the

air, and sometimes from the pigment itself, if reducible. Thus chromates are apt to turn green in oil. The unscientific use of driers is a fruitful source of destructive action, and where the composition of siccatives is unknown they should be regarded with suspicion. Water-colour is necessarily free from this danger, for the drying of water-medium is simply a question of evaporation and the solidification of dissolved gums, and no chemical change takes place; so that, assuming proper pigments to have been selected, it is probable that Ruskin (agreeing with Sir J. D. Linton) was right when he said that 'properly taken care of, as a well-educated man takes care of his books and furniture, a water-colour drawing is safe for centuries.'

4. *Action of pigments on each other.* Since little if any chemical action is set up by solid substances acting on each other, it follows that little if any change is effected by two pigments being immersed in a medium, provided these are insoluble in that medium. As, however, few pigments are absolutely insoluble, the least possible mixing of colouring matters is to be preferred. Consequently, the practice of grinding pigments with each other, whereby chemical action is facilitated, is more dangerous than the plan of mixing such pigments on the palette. At the same time, most of our pigments being inorganic, are soluble in water rather than in oil; so that oil is preferred as the medium which will best isolate the particles, whilst turpentine, on account of its greater fluidity as compared with oil, reducing the value of oil as an isolating agent, is sparingly used. It is recommended, therefore, in practice, with a view to permanence, that a copious supply of different pigments should be chosen rather than an excessive reliance on the mixture of a few.

III. ORIGIN.

1. *Pigments of mineral origin.* This class comprises: (A) Native earths, such as ochres, umbers, and siennas. They are of great durability and require no preparation except washing, grinding, and, in some cases, calcining. (B) Artificial pigments by the dry process—*i.e.*, by the action of heat—such as the vermilions, cadmiums, cobalt, smalt, &c. (C) Artificial pigments by the wet process—*i.e.*, by precipitation from aqueous solutions—such as aureolin, chrome yellows, emerald green, white lead, &c.

2. *Pigments of animal origin.* This class comprises such colouring matters as carmine and the lakes obtained from the cochineal insect; Indian yellow, or euxanthate of magnesia, derived from the urine of cows which have been fed on mango leaves (*v.* INDIAN YELLOW), gallstone, sepia, &c.

3. *Pigments of vegetable origin.* These are chiefly lakes. A *lake* is a pigment prepared by precipitating an animal or vegetable colouring matter in combination with a metallic base, usually alumina (*v.* LAKES). A *carmine* is that lake which, in comparison with others prepared from the same colouring matter, contains the greatest proportion of colouring matter to metallic oxide—as, *e.g.*, cochineal carmine, madder carmine, &c., &c. Indigo, madder lakes, brown pink, yellow lake, and Italian pink are obtained from the glucosides, indican, rubian, rhamnin, and quercitrin respectively.

IV. CLASSIFICATION UNDER COLOURS OF PIGMENTS IN ORDINARY USE.

White.

Lead whites.—The principal lead whites are: *Flake white*, *Cremnitz* or *Kremnitz*, *Crems* or *Krems white*, and *blanc d'argent*, which are all carbonates of lead, and always contain more or less of hydrated oxide of lead. Pure carbonate of lead is opaque and beautifully white, but has no great covering power. It also dries rather slowly. The presence of the hydrated oxide greatly increases its value as a pigment, since it combines with the oil to form an elastic, rapidly-drying varnish. On the other hand, the opacity of the paint is decreased. It is considered that the proportion of hydrated oxide should be about 25 p.c. The white leads are superior to all other whites in point of colour and body, but unfortunately they are open to the action of sulphuretted hydrogen. They are less liable to this action when exposed to strong light; and, if tarnished by that gas, are restored to whiteness by exposure to strong light. This is the effect of oxidation, whereby the black sulphide of lead becomes the white sulphate of lead. In the same way water-colour drawings in which the white has gone black may be restored by treatment with a solution of peroxide of hydrogen (*v.* LEAD).

Zinc whites comprise *zinc white* and *Chinese white.*

Zinc white is either the anhydrous oxide, the hydrated oxide, or the hydrated basic carbonate of zinc. It does not approach white lead in opacity, but may be relied on for permanence, and, unlike white lead, it is innocuous.

Chinese white was introduced in 1834, and supplied a want which was greatly felt by water-colour painters. It is a preparation of oxide of zinc, which works and washes well, and is beautifully white. It is not equally efficacious in oil.

Permanent white or *constant white* is sulphate of barium. It is a fair water colour, but is not so satisfactory in oil. It is permanent and innocuous.

Red.

Vermilions.—Native vermilion, which is mercuric sulphide—and occurs as *Cinnabar* in California, Peru, Spain, and China—is now commercially obsolete. Vermilion can be made both by wet and dry processes, the latter being the method usually adopted. It is prepared either of a deep or pale colour. It is permanent, and is eligible either in water, oil, or fresco, but cannot be used in enamel, as it is volatile at a red heat. It possesses great body, weight, and opacity, and in its best kinds is of a powerful vivid colour and more brilliant than all reds except the scarlet mercuric iodide.

Scarlet vermilion, *extract of vermilion*, *Chinese vermilion*, *orange vermilion*, and *Field's orange vermilion*, are all similar preparations varying somewhat in hue and transparency.

Pure scarlet is mercuric iodide. It has all the body and opacity of vermilion, and is as much inferior to it in permanence as it is superior in brilliancy. It cannot be mixed with other metallic pigments without being utterly destroyed. It is rapidly blackened by sulphuretted hydrogen, and [illegible] when exposed to light and air.

Red chrome is a basic chromate of lead. It is a good drier, but is blackened by sulphuretted hydrogen.

Mars red, or [illegible] *Mars*, is an artificial iron ochre, very permanent, but requires to be used cautiously with pigments affected by iron.

Light red is an ochre of orange russet hue. It is prepared by calcining Oxford ochre. It dries well, and is permanent.

Venetian red is sesquioxide of iron, and is prepared by calcining ferrous sulphate. It is very permanent, but, like Mars red, should be cautiously employed with pigments which are affected by iron.

Indian red, once called 'Persian red,' is brought from Bengal. It is a natural earth, rich in peroxide of iron. It is very permanent, and a good drier.

Red ochre is one of the most ancient pigments. It is a native earth, and is perfectly permanent.

Cochineal lakes consist of the colouring matter of the female cochineal insect precipitated on an aluminous base. The colouring matter of the cochineal insect is not in a free state, but exists in the form of a glucoside called *carminic acid*. By the action of acids, carminic acid may be split up into carmine red and glucose [illegible].

Carmine is that preparation of cochineal which contains the most colouring matter, and the least aluminous base. Hence it is the richest, deepest, and most intense of the cochineal lakes; but is probably not, as usually stated, the most permanent. It is, however, fairly stable under favourable conditions; but it will not stand in tint with white lead, and in glazing, though little affected by impure air, it is soon discoloured and destroyed by the action of light.

Crimson lake is a cochineal lake containing more aluminous base than carmine. Like all the cochineal pigments, it is affected by strong light and ultimately decolourised. It is a bad drier.

Scarlet lake is crimson lake with a scarlet hue imparted to it by a mixture of vermilion. It is not so permanent as crimson lake, since vermilion has a destructive action on cochineal lakes.

Madder lakes are prepared by precipitating the root of the madder plant, *rubia tinctorum*, with alumina.

Madder carmine is that preparation of madder which contains the greatest amount of colouring matter, and the smallest amount of base. It is the only durable carmine, either in water or in oil.

Rose madder is less intense than the preceding, and without its carmine hue. It is not liable to change by the action of light or impure air. It dries slowly in oil, and in water is inferior to cochineal so far as relates to working.

[illegible] synonymous with rose madder.

Indian lake or *lac lake* is obtained from the *lac* or *lacca* of India, a resinous secretion. It is more durable than cochineal, less durable than madder.

Dragons' blood is a resin from the East Indies. Its colour is deepened by impure air, and darkened by light. White lead soon destroys it, and in oil it dries badly (*v.* Resins).

Orange.

Cadmium orange is an exceptionally brilliant and lustrous pigment. It is a simple original pigment, containing no base but cadmium; and is perfectly permanent, being quite unaffected by exposure to light, air, damp, or sulphuretted hydrogen; or by admixture with other pigments.

Chrome orange or *orange chrome* is, like chrome red, a basic chromate of lead. It is characterised by want of permanence, and a tendency to injure organic pigments; and, by reason of its lead base, is apt to be discoloured by sulphuretted hydrogen.

Mars orange is an artificial oxide of iron, and being more chemically active than the native ochres needs to be cautiously used with pigments affected by iron. It is very permanent and dries well.

Burnt sienna is prepared by calcining raw sienna, of which it possesses all the properties, being, however, richer, and working and drying better. It is very permanent, although it is supposed to have a slight tendency to darken by time.

Burnt Roman ochre is obtained by calcining a very bright Roman ochre, whereby it acquires transparency and depth of colour. It dries and works well both in water and oil, and is very permanent.

Neutral orange, or *Penley's neutral orange*, is a permanent compound pigment composed of cadmium yellow and Venetian red.

Yellow.

Aureolin or *cobalt yellow* is a comparatively recent addition to the list of yellow pigments, and is a double nitrite of potassium and cobalt. It is permanent, being entirely unaffected by sulphuretted hydrogen, and, even in its faintest tints, is unaltered by exposure to the direct rays of the sun for a lengthened period. With all other colours it mixes safely and readily (*v.* Cobalt).

Cadmium yellows are sulphides of cadmium, and are consequently unaffected by sulphuretted hydrogen. They comprise deep cadmium and pale cadmium.

Deep cadmium is permanent, both with respect to sulphuretted hydrogen and exposure to light and air. It has been stated that the colour is destroyed by white lead. In theory this might be supposed to happen; in practice, if the cadmium is carefully prepared and free from excess of sulphur, it does not. In fact, it is found that a mixture of equal weights of cadmium yellow and white lead will withstand an atmosphere of sulphuretted hydrogen which completely blackens the white colour.

Pale cadmium is pale only relatively to deep cadmium, to which it is similar in chemical properties.

Deep chrome and *chrome yellow* are chromates of lead, which lose colour in time, and become black in atmospheres containing sulphuretted hydrogen.

Citron yellow is chromate of zinc. It is not affected by sulphuretted hydrogen, but fades on exposure to light and air. The affinity of the chromic acid for the base being small, the acid is liable to separate, and by deoxidation to become converted into green oxide of chromium.

Strontian yellow was originally a chromate of strontium, and as such is now obsolete; a pigment resembling it in colour and more durable in character being now sold under the same name.

Lemon yellow and *pale lemon yellow* are essentially chromates of barium. Properly and carefully-prepared chromate of barium is the only perfectly permanent chromate. Both of these colours work well in oil and water. They are not liable to change by the action of damp or foul air, by exposure to light, by contact with the steel palette knife, or by mixture with white lead and other pigments. Being uninjured by lime they are eligible in fresco.

Orient yellow resembles a brilliant and somewhat opaque Indian yellow, stands well in oil, and is quite unaffected by sulphuretted hydrogen. It cannot be used in water-colour.

King's yellow or *orpiment* is arsenious sulphide. Although not affected by sulphuretted hydrogen, it is not durable either in water or oil. It is destroyed by being mixed with lead colour, and is highly poisonous.

Naples yellow was formerly a compound of the oxides of lead and antimony. What is now sold under that name is a compound pigment, perfectly durable and trustworthy.

Mars yellow is an artificially-prepared iron ochre, of the nature of raw sienna. Like the ochre, it is absolutely permanent, and is a good drier; but it is more chemically active and should be used cautiously with pigments likely to be affected by iron.

Raw sienna is a ferruginous native pigment; not liable to change by light, time, or impure air. It may be employed in oil, water, or fresco.

Yellow ochre, *Roman ochre*, *transparent gold ochre*, *brown ochre*. These ochres are native earths, consisting chiefly of silica and alumina, coloured by sesquioxide of iron; and are less chemically active than the artificial iron colours. They are permanent, and may be safely mixed with pigments which are themselves permanent. They are especially adapted for fresco.

Yellow carmine, *Italian pink*, *yellow lake*. These pigments, comprised under the class of quercitron lakes, are prepared by precipitating the glucoside *quercitrin* contained in the bark of the oak *quercus tinctoria* with alumina. They are sensitive to light, and dry rather badly.

Gamboge is principally obtained from *Garcinia Hanburyi* found in Cochin China and Siam. It is a gum-resin which exudes from the wounded leaves and young shoots (*v. Gamboge*, art. GUM RESINS). Gamboge is a bright transparent yellow, but has no great depth. In its deepest touches it shines too much and verges on brown.

When properly used it is more durable than is generally reputed both in water and oil, and when mixed with other colours conduces to their stability. It is deepened to some extent by impure air, and somewhat weakened by the action of light. In water it works remarkably well, but is with difficulty employed with oil in the dry condition.

Gamboge may be rendered diffusible as an oil colour by forming it into a paste with water, and mixing it with lemon yellow. The best method is, however, to combine it with alumina (Field).

Extract of gamboge is a compound of gamboge and alumina.

Indian yellow (*v.* INDIAN YELLOW and PURREE). This pigment resists the sun's rays with singular power in water-colour painting; yet in ordinary light and air, or even in a book, the beauty of its colour is not lasting. In oil, both alone and in tint, it is decidedly fugitive; and, owing to its alkaline nature, injures carmine and cochineal lakes.

Gallstone. True gallstone is an animal calculus formed in the gall-bladder of oxen. It cannot be depended on for permanence, being destroyed by strong light, although not affected by impure air. It cannot be used in oil.

Green.

Oxide of chromium or *opaque oxide of chromium.* This and the two following varieties of sesquioxide of chromium vary from each other according to the mode of preparation. They are all strictly stable, being unaffected by exposure to light, air, or sulphuretted hydrogen. They neither act nor are acted upon by other pigments; they dry well, and are used either in oil or water.

Transparent oxide of chromium, being very deficient in body, is only eligible in oil.

Viridian or *French Veronese green*, is the hydrated sesquioxide of chromium containing two molecules of water. It is admissible in fresco; but cannot be employed in enamelling, since its very rich deep colour depends on the water of hydration, which is expelled by strong heat.

Emerald green is an aceto-arsenite of copper. It is the most durable of the copper greens, being unaffected to an appreciable degree by damp or by ordinary impurities of the atmosphere. It works much better in water than in oil, and dries with difficulty in the latter (*v.* ARSENIC).

Malachite green consists of hydrated cupric carbonate. It withstands the action of light and air, but, in common with the other non-arsenical copper colours, it is blackened by the combined action of damp and sulphuretted hydrogen.

Verdigris is a subacetate of copper. It is the least durable of copper greens. As a water-colour it soon fades by the action of light and air, and is very susceptible to damp and sulphuretted hydrogen. In oil it is permanent with respect to light and air; but moisture and an impure atmosphere change its colour, and cause it to effloresce. In varnish it stands better. It is a good drier.

Chrome greens or *Brunswick greens* or *Cinnabar greens* are compounds of chrome yellow and Prussian blue. Since chromate of lead ultimately destroys Prussian blue, these compounds should be avoided.

Hooker's green is a compound of Prussian blue and gamboge, which are innocuous to each other.

Prussian green is composed of Prussian blue and gamboge, the former being largely in excess.

Sap green is a pigment of vegetable origin, and is prepared from the juice of buckthorn berries, the green leaves of woad, &c. It is a fine natural yellowish-green. It is, however, a very imperfect pigment, disposed to attract atmospheric moisture, and to become mildewed. It has little durability in water and less in oil.

Terre verte is a species of ochre containing silica, protoxide of iron, magnesia, potash and water. It resists light and impure air, and combines safely with other colours. It has not much body, is semi-transparent, and dries well in oil. It has a tendency to grow slightly darker in course of time.

Cobalt green or *Rinmann's green* is a mixture of the oxides of zinc and cobalt. It is permanent, both alone and compounded; but is extremely deficient in body and power, and is now seldom used (*v. Cobalt green*, art. COBALT).

Blue.

Genuine ultramarine or *Native ultramarine* or *Real ultramarine*, one of the most permanent of pigments, is obtained by isolating the blue colouring matter of the *lapis-lazuli*, a stone brought chiefly from China, Thibet, and the shores of Lake Baikal. This colouring matter consists essentially of silica, alumina, sulphur, and soda, the characteristic colour being probably due to a compound of sodium sulphide and sodium thiosulphate.

Genuine ultramarine is prepared from the stone by separating the blue from extraneous matter, and yields first a deep and rich product, then a paler one, and lastly a bluish gray, which is known as *Ultramarine ash*. The refuse, containing little or no blue, furnishes *Mineral gray*.

It is transparent in all shades, is not injured by damp, by impure air or by the intensest action of light, remaining unimpaired in the oldest paintings. It dries well, works well in oil and fresco, and may be safely compounded with all other pigments. It does not work so well as some other blues in water, where it has a disposition to separate from other pigments.

Artificial ultramarines comprise *Brilliant ultramarine*, *French ultramarine* or *French* [illegible] are darker, less azure, and far less transparent than the natural varieties.

Cobalt blue or *Thénard's blue* is obtained by calcining a mixture of alumina and basic phosphate of cobalt. Although not possessing the body, transparency, and depth of ultramarine, it works better in water. It resists the action of light, but, by the attacks of impure air, it is in time greened and ultimately blackened. It dries well in oil, does not injure or suffer injury from other pigments, and may be used in enamel and fresco (*v. Cobalt blue*, art. COBALT).

Cœrulean blue or *Cœruleum* is a stannate of cobalt. It possesses the distinctive property of appearing a fairly pure blue by artificial light, for which reason it is admirably adapted for scene-painting, whilst for other purposes it is surpassed by some other blues.

Smalt is a double silicate of cobalt and potassium. It is a vitreous compound, and is a vivid violet blue; but rapidly deteriorates either in water or oil (*v. Smalt*, art. COBALT).

Prussian blue was discovered in 1710 by Diesbach, a colour-maker of Berlin. It consists essentially of ferro-cyanide of iron. It dries well in oil, and although not permanent will last a long time under favourable circumstances. It fades under the action of a strong light; but regains its colour in the dark, possessing the singular property of fluctuating according as its position is favourable to acquire or relinquish oxygen. It is darkened and discoloured by damp and impure air, and cannot be employed in fresco, as it is destroyed by alkalis, nor in enamel, as it cannot withstand high temperature (*v.* CYANIDES).

Antwerp blue is a compound of Prussian blue with alumina.

Cyanine blue or *Leitch's blue* is a mixture of cobalt blue and Prussian blue. It gradually fades to the hue of the more permanent cobalt.

Indigo, or *Indian blue*, is derived from the glucoside *Indican* existing in the leaves of various species of *Indigofera* native to India, Africa, and America. The leaves, being fermented in water, the indican is decomposed to indigo blue and glucose. Indigo is extremely powerful and transparent; has great body and works well in water and oil, but it is very fugitive and impure air injures it (*v.* INDIGO).

Intense blue is indigo refined by solution and precipitation, and is more durable, powerful, transparent, and deep.

Purple.

Purple madder is a lake formed by precipitating the colouring matter of madder in combination with a metallic oxide. It is the most useful, and, with one exception, is the only permanent purple pigment. It has great transparency and body, and it neither injures nor is injured by other pigments. It dries and works well in oil and may be used in fresco.

Purple lake in its general properties resembles crimson lake, but it is more durable.

Burnt carmine is obtained by partially charring carmine.

Burnt lake is partially charred crimson lake. It is less permanent than burnt carmine.

Indian purple is prepared by precipitating cochineal extract with sulphate of copper. It is apt to blacken on exposure to light and air.

Violet carmine is obtained from the root of *Anchusa tinctoria.* On exposure to light and air it loses its colour and blackens.

Mars violet is an oxide of iron. It resembles Indian red in body, opacity, and general properties. It is very permanent, and dries [illegible].

Brown.

Brown madder is a lake prepared from the madder root; very permanent, dries and works well, and altogether is an excellent pigment.

Rubens madder is also a preparation of madder with similar properties to the preceding, except that it does not dry well in oil.

Bone brown is obtained by partially charring ivory dust. Although much esteemed by artists as an oil-colour only, it is a bad drier, and will not withstand the action of strong light.

Bistre is used only in water-colour. It is prepared from the soot of wood. It is durable, but has a tendency to absorb moisture from the atmosphere.

Prussian brown, a compound of sesquioxide of iron and alumina, is transparent, permanent, and a good drier.

Burnt umber is prepared by calcining raw umber. It works well, dries well, and is perfectly stable. It is also eligible in fresco.

Verona brown, used only in oil-painting, is a calcined ferruginous earth.

Vandyck brown is a species of bog-earth, and is semi-transparent. The pigment used by Vandyck was an earth brought from Cassel. The modern Vandyck brown is a purified bituminous ochre. It is durable in both water and oil, but dries badly in the latter.

Caledonian brown is a permanent native pigment, used only with oil. It possesses considerable transparency, richness, and depth.

Cappagh brown, used only in oil-painting, is a species of bog-earth, containing peroxide of manganese. It possesses more or less richness and transparency. It works well in oil and varnish, dries quickly, but does not retain its place.

Cologne earth, originally a native bituminous earth, is now prepared by calcining Vandyck brown, which it resembles in general properties.

Asphaltum or *bitumen*, originally a variety of pitch obtained from the Dead Sea, is now prepared by distilling resinous and bituminous matter, and is procured in great abundance as a by-product in the manufacture of coal-gas. It is chiefly confined to oil-painting, but is not a desirable pigment, since it contracts and cracks under changes in temperature and atmospheric conditions; and it has a tendency to blacken. The solution with turpentine is called *asphaltum*; the mixture with drying oil, *bitumen*; and a preparation for water-colour is known as *liquid asphaltum*.

Mummy varies exceedingly in its composition and properties, and is little to be relied upon. It is a bituminous product mixed with animal remains brought from the catacombs, where bitumen was employed in embalming. It resembles asphaltum, but is less liable to crack. Used only in oil.

Sepia is obtained from the cuttle-fish (*sepia officinalis*), all species of which are provided with a dark-coloured fluid, which they emit to obscure the water as a means to conceal their movements. The liquid consists of a mass of extremely minute carbonaceous particles mixed with an animal gelatine. Sepia is a powerful brown of fine texture; it is transparent, works admirably in water, combines well with other pigments, and is very permanent. It cannot, however, be used as an oil-colour, as it dries very slowly.

Warm sepia is sepia 'warmed' by mixing it with redder browns.

Roman sepia similarly is sepia mixed with yellow browns.

Citrine and Olive.

Brown pink, or *Stil de Grain*, is generally prepared from Avignon berries (seeds of *Rhamnus infectorius* and *R. alaternus*), or from Turkey and Persian berries (*Rhamnus amygdalinus*; *R. oleoïdes*), but is sometimes made from quercitron bark. If produced from the berries it is fugitive; if from the bark it is somewhat more stable. In either case it is a lake precipitated by alum from a decoction of the colouring matter containing a great excess of alkali. The colouring matter has been called *rhamnetin*, and exists in the glucoside *xanthorhamnin*. Brown pink possesses much richness and transparency, and works well in both water and oil; but it does not stand well, and is very fugitive with white lead. The variety made from berries also dries badly.

Raw umber is a natural ochre, and is a hydrated silicate of iron, manganese, and alumina. It is semi-opaque, dries rapidly, and does not injure other pigments.

Mars brown is either a natural or artificial ochre, containing iron or iron and manganese. It is strictly permanent.

Olive lake, originally prepared from green ebony, is now exclusively a mixture which is semi-stable and liable to blacken.

Olive green, or *De Wint's green*, is a compound of variable composition, and cannot therefore be said to possess uniform characteristics. Generally speaking, it is decidedly fugitive.

Gray.

Ultramarine ash, a by-product in the preparation of ultramarine from the *lapis-lazuli*, varies considerably in tone.

Mineral gray, also a by-product of the manufacture of ultramarine, possesses the permanence of that blue. Its use is confined to oil-painting.

Neutral tint and *Payne's gray* have a tendency to become *grey* as opposed to *gray*, the former term being employed to denote a mixture of black and white, the latter term being applied to any broken colour of a cool hue.

Black.

Ivory black is obtained by charring ivory in closed retorts. It is the richest and most transparent of all blacks, is perfectly durable, and may be used in both water and oil. It is found, however, to vary in hue and intensity, according to its preparation. As ivory black is nothing more or less than an animal charcoal, it should not be brought into contact with organic pigments. In compounding colours, therefore, lampblack and blue-black should be employed.

Lampblack (*v.* LAMPBLACK) forms a pigment of fine texture and strong body. It works well, but dries badly.

Blue-black is a charcoal prepared from vine-twigs. In common with all carbonaceous blacks, it has a preservative influence on white lead. A mixture of these washed over with zinc white may be said to be practically permanent.

Cork black is a soot obtained by charring cork.

Indian ink (*v.* INDIAN INK or CHINA INK) is another form of carbonaceous black.

[illegible] any colour, and is strictly permanent.

[illegible] Colours'; Von Bezold, 'Colour in its Relation to Art and Art Industry'; A. H. Chevreul, 'Colour'; P. G. Hamerton, 'Practical Work of Painting'; Helmholtz, 'Relation of Optics to Painting'; Helmholtz, 'Physiological Optics'; 'Field's Chromatography,' by T. W. Salter; 'Field's Chromatography Modernised,' by J. Scott Taylor; Rood, 'Modern Chromatics' in the International Series; Standage, 'The Artist's Manual of Pigments'; Jno. Collier, 'Primer of Art'; Chevreul, 'Laws of Contrast of Colour.'

PILOCARPENE, PILOCARPIDINE, PILOCARPINE *v.* JABORANDI.

PIMARIC ACID *v.* RESINS.

PIMENTHOL *v.* CAMPHORS.

PIMENTO OIL [illegible]

PINCHBECK. An alloy of zinc and copper [illegible] in the latter part of last century. It was for[illegible] cases, and other small ornamental articles in imitation of gold. Its composition is variable, but usually consists of 9 parts of copper to 1 part [illegible]

PINE OIL *v.* OILS, ESSENTIAL.

PINE RESIN [illegible]

PINUS SYLVESTRIS OIL [illegible]TIAL.

PIPE-CLAY *v.* CLAY.

PIPERIC ACID *v.* RESINS.

PIPERIDIN *v.* RESINS.

PIPERIDINE *v.* BONE OIL.

PIPERINE [illegible]

PITCH. Various substances met with in the organic kingdom when submitted to destructive distillation, yield, in addition to fluid products, a residuum that on cooling assumes a more or less viscous or solid character; and, furthermore, at various places on the earth's surface extensive deposits are found consisting of black, resinous substances of similar appearance and properties. To these products have been assigned the terms of 'pitch,' 'bitumen,' and 'asphaltum.' Each of these substances possesses distinctive features, and each in its place fulfils important requirements in the arts.

Bitumen, asphaltum, mineral pitch. These compounds consist of complex mixtures of hydrocarbons, and are found in many localities and under the most varied conditions. Probably the celebrated Pitch Lake, situate in the Island of Trinidad, and said to be upwards of three miles in circumference, represents one of the most important deposits of natural bitumen known, although within the past thirty years many additional sources have been found in Cuba, Central and South America, California, Nicaragua, and Peru; in India, Palestine, Egypt, Italy, [illegible] province of Szu-Tchuan, China.

The origin of these compounds is involved in considerable obscurity; they appear to have been formed by the oxidation of the unsaturated hydrocarbons in petroleum. Bitumen has been regarded as either a product of chemical action, or as a distillate produced by natural causes from animal and vegetable remains. It has been argued that if the bitumen were the result of a purely chemical process, we should expect to find a general uniformity in the character of the substance wherever found on the earth. On the other hand, if petroleum is the result of metamorphism, its generation is co-existent only with that of metamorphic actions. If we accept this hypothesis, the generation of petroleum must be considered as practically ended.

In studying the asphalts of Bentheim, Patrono, Castro, Colla San Magna, and other places, the conclusions arrived at have confirmed the views of Mendeléeff to the effect that their formation has been brought about by inorganic means. Bitumen is frequently met with in places where, from a geological point of view, its occurrence can be explained only by assuming that it has accumulated within the fissures in the same manner as that contained in lavatic geodes, and separated from prehistorical tufaceous deposits by inorganic means. Engler, who has given some considerable study to the Bentheim asphalt, furnishes the following par[illegible]:

Sp.gr. 1·092. It is insoluble in alcohol, ether, carbon bisulphide, oil of turpentine, and similar solvents, but melts when strongly [illegible].

It contains:

	I.	II.
Carbon . . .	89·16	89·83
Hydrogen . . .	9·55	9·88
Ash	1·09	1·14

Distillation yielded the following products:

	I.	II.
T[illegible]	[illegible]	[illegible]
Coke	48·9	48
Gas and water . . .	14·3	14

The tar had a sp.gr. of 0·834, forming a thick semi-liquid mass, and yielding the following fractions when subjected to distillation:—

At 150°, 10·3 p.c. oil; sp.gr. 0·743.

At 150-310°, 93·3 p.c. burning oil; sp.gr. [illegible]

Residue, 46·4 p.c.

The tar obtained by the distillation of the asphalt on a large scale was free from phenol and creosotic compounds, and the products of its distillation were as follows:

Burning oils . .	12·72
Gas and lubricating oils . .	9·78
Paraffin	[illegible]
Paraffin grease . .	[illegible]
[illegible] . .	45·09
Coke from tar . .	[illegible]
Pitch	1·52
Loss, gas and water . . .	25·88

[illegible]:

Carbon	[illegible]
Hydrogen	[illegible]
Oxygen	[illegible]
Nitrogen	0·25

The bitumen of Judea, found floating on the Dead Sea, contains:

Carbon	77·84
Hydrogen	8·93
Oxygen	11·54
Nitrogen	1·70

Sulphur is invariably present in natural bitumens, varying in quantity from 3 to 4·2, and even 10, p.c.; from such samples hydrogen sulphide is always given off on heating. Asphaltums and bitumens vary considerably in character; generally speaking their appearance is that of smooth, hard, brittle, black or brownish black resins, breaking with a distinct conchoidal fracture; the sp.gr. varies from 1 to 1·7; when free from mineral matter they may be even lighter than water. When distilled with water, asphaltum yields a volatile oil called by Boussingault 'petrolene,' probably consisting of a mixture of paraffins. The residue of 'asphaltine' which remains when the petrolene is completely driven off, is a solid black substance resembling the original substance prior to distillation, but which does not soften under about 300°C., and decomposes below its fusing point.

Trinidad pitch yields when heated:

Volatile organic matter . .	76·75
Non-volatile organic matter .	17·77
Ash	5·48
	100·00

Natural bitumen is only partially soluble in alcohol, but more completely so in carbon bisulphide, petroleum spirit, chloroform, oil of turpentine, coal-tar, benzol, and naphthas; the pyridine bases, also derived from coal-tar, scarcely act upon it. The portion, however, that passes into solution communicates a strong greenish fluorescence to the liquid, and when examined spectroscopically, in the manner pointed out by the writer in examining crude anthracenes for certain impurities (C. N. 26, 199; 31, 35, 45), two distinct absorption bands are visible near the D line of the spectrum, from yellow to green, which distinguishes it from all other pitches, coal-tar excepted, which occasionally exhibits bands, but invariably situate in the blue portion of the spectrum near the F and G lines.

In petroleum spirit 74·23 p.c. of its organic matter is soluble, and 20·29 p.c. insoluble.

At a temperature varying from 58° to 60°C. bitumen softens, and melts at about 100°C., although varieties are met with that melt only at a much higher temperature.

Applications of asphaltum.—The purer asphaltums are employed almost exclusively for the manufacture of black varnishes and japans, for which purpose they are eminently adapted, yielding surfaces and coatings of great brilliancy and not prone to 'break up' or disintegrate. Asphaltum selected for the purposes of the varnish maker should be practically free from mineral matter or within a limit of 5 p.c., it should be completely soluble in carbon bisulphide, chloroform, high boiling-point coal-tar naphtha, and oil of turpentine (mineral matter excepted). It should break with a conchoidal fracture, and brilliant lustre. It should not flow or lose shape, like wood tar and many of the fatty pitches, when left on a plane surface, and an angular fragment should retain its shape and the sharpness of its angles in boiling water.

Asphalt rock. Asphaltum is often met with associated with sand or limestone or the two variously admixed; for this condition the mineral is known as 'asphalt rock,' and occurs in the upper Jurassic formation introstratified with ordinary limestones.

The following figures, by M. Durant Claye, show the proximate composition of some rock asphalt employed for paving:—

—	Val de Travers, Switzerland	Lobsann, Alsace	Seyssel, Ain, France	Maestu, Spain	Ragusa, Sicily
Water and other matters volatilised at 100°C.	0·35	3·40	0·40	0·40	0·80
Bituminous matter	8·70	11·90	9·10	8·80	8·85
Sulphur, in organic combination or free state	0·08	4·99	—	trace	—
Iron pyrites	0·21	4·44	—	—	—
Alumina and oxide of iron . .	0·30	1·25	0·05	4·35	0·90
Magnesia	0·10	0·15	0·05	3·85	0·45
Lime	49·50	38·90	50·50	5·70	49·00
Carbonic acid	40·16	31·92	39·80	8·15	39·40
Combined silica	—	—	—	11·35	—
Sand	0·60	3·05	0·10	57·40	0·60
	100·00	100·00	100·00	100·00	100·00

Native calcareous asphalt exhibits a brown or nearly black colour, and breaks without evidence of cleavage. The fracture is earthy and granular, not unlike chocolate both in appearance and colour. When long exposed to the air it loses this character, and then resembles ordinary limestone; this change, however, only extends to the surface.

The specific gravity of rock asphalt is about 2·23. It is hard and may be broken with a hammer, but when warmed it may be softened to a kind of paste, and at about 60° falls to powder.

Good asphalt rock is homogeneous in structure, and shows no indication of contained limestone. It is frequently veined, and contains large crystals of calcite impregnated with bitumen; this feature is considered an important indication, bad specimens, or low qualities, showing an absence of such impregnation which renders them difficult to manipulate. Val de Travers, Seyssel, and other asphaltic rocks, when employed for paving, are melted with definite proportion of good native material, such as Trinidad pitch. The product of this mixture is technically known as 'mastic,' and in using it further additions of bitumen, shale oil, and grit are frequently made.

The following analyses are by M. Durant Claye, and will convey a general idea of these compositions:—

—	Refined bitumen from Bastennes	Squeezed asphalt made with Bastennes bitumen	Imitation asphalt made from coal tar
Moisture	0·30	0·15	0·60
Bituminous matter soluble in carbon bisulphide	69·35	84·05	20·65
Organic matter insoluble in carbon bisulphide	4·10		18·45
Alumina and oxide of iron	2·85	0·85	2·65
Magnesium and calcium carbonates . .	2·65	80·40	39·60
Silica	20·35	1·55	18·05
	100·00	100·00	100·00

For determining the actual bituminous matter in asphaltic rocks, natural or otherwise, the air-dried sample is exhausted with suitable solvents, which may consist of carbon bisulphide, Russian oil of turpentine or coal-tar benzene. The operation may be conducted in a Soxhlet's tube, and if a correction be made for the moisture expelled at 100°C. the loss of weight furnishes the quantity of bitumen removed. The determination may be further checked by distilling off the solvent, and weighing the residue, observing the usual precaution of drying at 100°C. till constant. The bitumen thus obtained should be further heated to 220°C., when if the sample is good, there will be little or no further loss; if, however, volatile oils or petroleum be present, the loss may be considerable. The volatile oil is best determined by repeatedly digesting the powdered sample with cold alcohol and weighing the residue; the exhaustion may be taken as complete when a portion of the alcoholic washing shows no turbidity on dilution with water.

If the residue left after exhaustion exhibits a dark colour, other organic constituents of valueless nature are present. Their proportion may be ascertained by igniting the weighed residue left after removal of the bitumen, re-carbonating it with ammonium carbonate, again gently igniting it, and re-weighing. The loss of weight represents the quantity of non-bituminous matter present.

Val de Travers asphalt gives up the whole of its organic matter to petroleum spirit, imparting a deep-brown colour to the fluid, perfectly free from fluorescence, whereas the soluble portion of coal-tar pitch does not exceed 20 or 25 p.c., yielding a solution exhibiting a deep-greenish fluorescence—a characteristic of this pitch in any of its solvents, and which renders its detection alone or in admixture a matter of no great difficulty (*v. infra*).

PITCHES DERIVED FROM VARIOUS PROCESSES.

Artificial pitches.—Coal-tar pitch may be looked upon as occupying the most prominent position in the series, both as regards the magnitude of its production and its corresponding consumption for the purposes of artificial fuel, asphalts, and varnishes.

Some idea of the extent to which this residue is produced in the United Kingdom, together with the industry springing out of it, may be gathered from the statement that from an annual distillation of coal-tar, varying from 100,000,000 to 120,000,000 gallons, and representing for the latter figures about 645,000 tons, pitch to the extent of about 396,000 tons is obtained, by far the larger portion of which is consumed in the manufacture of patent fuel.

Coal-tar pitch is the residue remaining in the stills after separation of the various fractions known as naphthas, light oils, carbolic, creosote, and anthracene oils, and amounts to about two-thirds of the weight of the tar operated upon. Its physical character is mainly dependent upon the temperature employed in distillation, but its ultimate chemical composition is more or less governed by the quality and description of coal distilled. It may be either 'soft' or 'hard' or 'medium'; it may be either normal, as a product resulting from the simple distillation of tar, or it may be otherwise, as when mixed with green or other tar oils before running from the stills, which represents the character of coal-tar pitch produced at the present period. The selection of tar distillates to be used in thus thinning down a pitch carried to a full limit of distillation is important, as it has been found that when creosote or naphthalene is employed, a pitch is obtained lacking in binding or cementing power, and blocks or briquettes made from it are liable to crumble. This defect is only obviated by the use of the heavier distillates, such as green oils, which are of a more viscid and adhesive character.

In the earlier days of tar distillation, the operation differed in not being carried to the extent now followed—that is to say, a much less quantity of anthracene oils was taken off: as a consequence of this, the resultant pitch was of a character not met with in the present day, or, if so, only within narrow limits and from the operations of small distillers. Pitch of this kind always contained a notable quantity of anthracene; hence it was more or less worked for the recovery of that substance, and the earlier literature of tar deals at considerable length with plans and patented processes for the treatment and distillation of pitch, specially for the recovery of retained anthracene, which at the period in question was of much greater commercial value than at the present time. These processes are now of historical interest only. They have given way to methods of distillation of the tar that yield a pitch practically free from anthracene, and hence valueless for the purposes of after-distillation.

About 48 p.c. of coke results from continuing the distillation of pitch to its 'coking point'; this coke has been regarded as of excellent quality for refining pig iron, and fusion processes in crucibles. It contains sulphur in small quantities only, varying from 0·1 to 0·13 p.c.; from absence of iron sulphides it does not crumble even after long exposure, and is said to surpass the best Durham coke in firmness, density, and heating power.

When pitch is passed through a red-hot tube it yields about 250 times its bulk of gases, chiefly hydrogen.

Pitch may be utilised by burning it into lampblack, and, according to Thenius, 500 kilos. of pitch yield 200 kilos of varying descriptions of lampblack and 200 kilos. of coked residue.

Referring more generally to the several results that may be obtained by varying the fractions during the distillation of coal tar, it may be stated that if the operation be terminated at the point at which the light oils only are driven off, the residue in the still, representing about 80 p.c. of the charge, may be, and has been, used for the preparation of asphalts, under the name of 'refined or prepared tar,' although it is very doubtful whether material of this character is to be met with in the present day. If about 10 p.c. more is run off, the residue is a soft pitch; moderately hard and hard pitch follow, the latter when the distillation is carried on as far as practicable in wrought-iron stills. The 'asphalt, prepared or refined tar' thus obtained by simply distilling off the naphthas and light oils, invariably contained all the constituents of the distillate that would follow if carried to its limit and collected apart—*i.e.* creosote oils, phenols, naphthalene, anthracene, and the higher boiling-point substances. Coal-tar pitch, in its normal condition and as originally obtained, is a bright, black, lustrous substance, breaking with a well-marked conchoidal fracture; but as now met with it presents a more or less dull and greyish tint, due to the altered condition under which it is obtained. These are, firstly, distillation in which steam, either superheated or otherwise, is injected into the still during the operation, and by which it can be pushed to a greater limit and more complete extraction of anthracene, without endangering the still; and, secondly, the admixture of the residual pitch with 'green' or other tar oils, in order to bring it to a consistency at which it may be run off with facility, and yield a product that shall represent 'soft, medium, or hard pitch,' at will.

The proximate composition of coal-tar pitch is by no means well understood. It invariably contains some of the high-boiling hydrocarbons of coal tar—notably anthracene, phenanthrene, pyrene, chrysene, together with bitumen and free carbon. The ultimate percentage composition of coal-tar pitch may be stated as

Carbon	75·32
Hydrogen	8·19
Oxygen	16·06
Ash	0·43

Small proportions of sulphur and nitrogen are also present, the former to the extent of 0·4 to 0·7 p.c. Treated successively with cold benzene, carbon bisulphide, boiling benzene, and boiling alcohol, Behrens obtained 23·54 p.c. of a black powder resembling anthracite, and containing 91 to 92 p.c. of carbon, 3·1 of hydrogen, and 0·4 to 0·9 of ash.

The specific gravity of hard pitch varies from 1·475 to 1·300. It is wholly insoluble in water, but partially soluble in alcohol, and more completely in benzene and carbon bisulphide; cold petroleum spirit exerts but little solvent action upon it, but when heated it dissolves it to the extent of 18 to 23 p.c. The pyridine bases also dissolve the soluble organic matter from pitch, but somewhat tardily, and only by the assistance of heat.

Solutions of coal-tar pitch exhibit a deep yellow or yellowish green fluorescence, which is highly characteristic of that substance. When heated it exhales an odour equally characteristic, and not easily mistaken for any other known pitch. The proportion of 'volatile organic matter' given off on heating ranges from 47 to 64 p.c.

A benzene solution of coal-tar pitch when examined spectroscopically shows a cutting-out of the blue and violet portions of the spectrum, with occasional absorption bands between the F and G lines, due to the presence of imidophenylnaphthyl.

Testing of pitch.—For the requirements of commerce pitch has to be tested for its 'softening and melting point,' and contract notes stipulate that a sample is to 'twist fairly after immersion for two minutes in water at 60°C., but not under 50°C.; must contain at least 53 p.c. of "volatile organic matter," and must be free from any extraneous matter, such as grit or sand.'

The twisting and melting point of pitch are ascertained by methods of comparative simplicity, only varying in trifling points and details. Probably the simplest and most readily followed is that of Mr. F. G. Holmes, of Messrs. Burt, Boulton, & Haywood, and is conducted in the following manner:—

Several pieces of pitch are selected from different parts of the sample, and cut to the size of half-inch cubes. These cubes are then supported on metal wires by heating the end of the wires and pressing them into the pieces of pitch, which are then suspended in a vessel containing about 500 cubic centimetres of water heated by any convenient means, at a uniform rate of 50°C. per minute, as indicated by a thermometer immersed in the water with the bulb about two inches from the bottom of the vessel.

The cubes are suspended on a level with the bulb of the thermometer; as the temperature rises the pieces of pitch are removed from time to time and twisted or squeezed with the fingers, and the temperature noted at which they assume the following conditions:—

(1) Readily twisting or soft—*i.e.* when the pitch can be easily twisted round several times.

(2) Very soft—*i.e.* when it yields to a very light pressure of the finger.

(3) Fused—i.e., when the pitch [illegible] the wire.

Soft pitch softens at 40 C., and melts at about 60 C.

Moderately hard pitch softens at 60 C., and melts at about 80 C.

Hard pitch softens at 80 C., and melts at about 120 C.

The estimation of volatile matter is conducted in the same way as that used in the case of coal and other bituminous substances – viz., by heating about 1 gram of the pitch to be examined in a platinum crucible [illegible] inches in depth, with the cover on, which should have a small aperture in its centre. The heat is applied by means of a good Bunsen burner, first gently, till no more smoke and vapour issue from the opening in lid, finally as strongly as the burner will permit. The operation may last twenty minutes. The crucible is then placed in a desiccator, and after cooling the residual coke is weighed; it ranges from 36 to 53 p.c.

Fixed carbon and coke-dust may be determined by successively exhausting with benzene, carbon disulphide, and alcohol, employing a Soxhlet tube for the extraction.

The suitability of a pitch for the purpose of artificial fuel may be ascertained by carefully distilling a given quantity of the sample in a glass retort and noting the character of the distillate; when creosote or naphthalene has been used in thinning or diluting before running from the still, they are accompanied with a considerable sublimate of naphthalene passing over at a comparatively low temperature; green oils do not yield naphthalene in this manner, or sublimates that may be mistaken for it.

APPLICATIONS AND USES OF COAL-TAR PITCH.

Coal-tar pitch is extensively used in the manufacture of patent or artificial fuel, varnishes, japans, and asphalts, the trade in the first-named product having assumed enormous proportions. Fuel of this description consists of admixtures of coal-tar pitch with small coal or slack, compressed into the form of blocks, and known in common under the name of 'Briquettes.' This industry would seem to be due to Ferrand and Marsais, [illegible] for using coal tar for this purpose. Marsais, since 1842, employed soft pitch, and in that year commenced the works at Bérard, near Saint Etienne. Hard pitch was used in 1843 in England by Wylam, and since 1854 in France. The manufactured fuel was sold in that country under the name of 'péras.' The manufacture of patent fuel has opened up wide channels for the consumption not only of the immense quantities of 'slack' obtained wherever mining operations for coal is carried on, but for the almost equally large bulk of pitch resulting from the operations of the tar distiller.

This industry has principally developed itself in France and Belgium, but it will be seen from the following tabular statement giving the 'output' of patent fuel, that other countries share in the production of this important article (Schultz, Steinkohlentheer, 2nd ed. p. 87): —

	No. of Works	Tons
France . . .	31	1,000,000
Belgium . . .	16	[illegible]
England . . .	7	300,000
Austria . . .	5	250,000
Germany . . .	4	200,000
Italy	3	150,000
Spain	3	100,000
Russia . . .	1	100,000
Sweden . .	1	
		2,600,000

The principal [illegible] of this industry [illegible] :

Swansea .	Graigola Merthyr Co. Atlantic Fuel Co. (Vivian & Co.)
Cardiff .	Star Fuel Works Crown Fuel Works
Newport .	Cardiff and Newport Fuel Co.
Sunderland	[illegible] Fuel Co. ([illegible] & Co.)

In the manufacture of briquettes certain conditions are observed, regulating shape, dimensions, and weight. The form should be that of a parallelopipedon, and they should not weigh more than 22 lbs.; they should possess a firmness approaching that of natural coal, and to attain this end the proportions of pitch used in their fabrication must be at least 5 to 7 p.c. They should not yield more than from 6·5 to 6·75 p.c. of ash, if intended for locomotive use, or 10 p.c. if for steamboat use. When broken they should fracture with a clean, bright and granular surface, in the absence of which they are generally faulty. Their regular shape permits of facilities in stowage, and the loss in transit by disintegration does not amount to more than 1 or 2 p.c. against 30 to 50 as with coals. They should not fall to pieces in the fire, but agglomerate into a firm, compact coke.

Patent fuel of good quality is said to yield 10 p.c. more heating power than steam coal, it makes less dirt, and when manufactured from hard pitch gives less black smoke than most kinds of coal. An advantage arising from the use of briquettes is that the exact consumption of fuel in a given work or operation is always known from the number of blocks used.

In the preparation of artificial fuel of this character numerous attempts have been made to employ fatty, oily, mucilaginous, and similar substances, or coal tar, as the agglomerating or cementing medium, but the only materials now used are soft and hard pitch derived from coal tar.

The operation of blending is comparatively simple, requiring little plant beyond that of melting-pans or pug-mills; occasionally, when hard pitch is employed, a mixture of this material with coal, both in fine powder, is subjected to the action of superheated steam, by which the compound is softened and yields a compact conglomerate on cooling.

In shaping or forming such mixtures of coal and pitch into blocks or briquettes, presses with open and closed moulds are in use; the process scarcely requires description, being quite analogous to that of moulding bricks, the machine that works with dry clay being constructed with closed moulds, those for wet clay with conical mouth-pieces (dies).

Within a comparatively recent period the use and consumption of artificial fuel has greatly increased, becoming more or less general for household consumption; so widely has its use extended in this direction that it is now to be met with in every town throughout the United Kingdom, and its consumption is no longer limited to the steam-boiler and the ocean steamship.

Black varnishes and japans. In the preparation of varnishes, japans, and paints for coating and protecting surfaces of iron and wood, tar pitch is simply dissolved in, or melted with, a suitable coal-tar distillate, depending on the purpose to which the product is to be applied and the rate at which it is required to dry or become hard. These solvents vary from the more volatile benzene to the heavier xylenes or solvent naphthas, and it is not an unusual thing to employ naphthas and light oils as run from the still, up to actual creosote; no special knowledge or plant is requisite in compounding them beyond that well known to varnish makers.

As a rule, the pitch should be melted at the lowest temperature, and the solvent in the first instance added in small quantities, after which it may be introduced more freely up to the desired consistency. Rosin in varying proportions is occasionally added, but in the majority of cases pitch alone is used. Varnishes so prepared will obviously vary in character, drying quality, and lustre, and it is hardly necessary to point out that when required of a nature that shall dry rapidly and with a bright uniform surface both the pitch and the solvent employed should be free from water. Tar varnishes dry with a bright and hard surface, and adhere both to wood and iron with considerable tenacity; they have been extensively employed for coating the hulls of iron ships, anti-fouling compositions, and for the purposes of protective paints generally.

Asphalts and compounds for paving. Asphalt prepared from substances derived from coal tar has found a wide application, especially for the purpose of street paving; surfaces of ground coated or covered with asphalte become impenetrable to moisture and the passage of noxious effluvia. Coal-tar asphalt may be regarded as a soft pitch to which body or firmness has been imparted by incorporating sand, grit, gravel, chalk, lime, and substances of a similar character; the soft pitch used for this purpose may consist of the residue from tar after distilling off the more volatile constituents, and known as refined or prepared tar, or it may consist of hard pitch, afterwards melted and thinned down to the required consistency with heavy tar oils, preferably green oils.

The manufacture of this pitch into asphalt suitable for street paving is carried on in various ways; occasionally the pitch is melted in iron pans, and the ingredients to be incorporated simply added and well stirred in; the mixture, containing 20 to 30 p.c. of pitch, is used while hot and in a plastic condition.

Asphalt, in the form of blocks or slabs, is manufactured for similar purposes, melted pitch being run direct into a pug mill, in which it is incorporated with the proper proportion of sand, gravel, or grit, and from this mill the mixture is run direct into sand moulds to harden and solidify.

Tar asphalt is said to be considerably improved by the addition of about 5 p.c. of sulphur, added in small portions at a time during the heating or melting; much sulphuretted hydrogen is given off, and it is thought that during the heating the sulphur decomposes the constituents rich in hydrogen, and thus renders the residue less fusible. Starting with a soft pitch or viscid tar, it is said 75 p.c. may be obtained as a good asphalt, which does not soften in boiling water. (The writer can confirm this assertion, having made and employed such sulphur compounds of coal tar to a considerable extent for the purposes of telegraphic insulation at the works of Mr. William Hooper, Mitcham, Surrey, in the year 1860.)

Coal-tar asphalt—or, more correctly, very soft pitch—is also employed for constructing 'asphalt pipes.' This industry was introduced by Jaloreau, and has been minutely described by Behrens (D. P. J. ccviii. 377). Endless hemp paper 7 feet wide is passed through a semi-cylindrical pan set in a furnace and filled with hot pitch. A roller revolving in the pan takes up the paper saturated with pitch and conveys it to a smaller roller forming the core of the pipe, round which any number of layers of paper may be wound. When the desired thickness has been attained fine sand is dusted on, and the cylinder is exposed to considerable pressure. After a cooling in water the core is withdrawn and the pipe becomes ready for use. Pipes manufactured in this manner resist very considerable pressure from within. They possess many features of value for special uses and are employed for conveying water, acids, air-blasts for pit ventilation, and for conveying underground telegraphic wires.

A tarred or asphalt paper is also manufactured for packing purposes, consisting of wrapping paper impregnated with soft pitch; another description consists of two layers of paper united by a coating of pitch, which has been used for papering damp walls.

A further and more important application of materials, such as paper and felts, saturated with 'prepared or refined tar,' or pitch let down to the required consistency by solution in heavy tar oils, is for the purpose of 'roofing paper or felt.' A considerable quantity of this material is manufactured in Germany and elsewhere.

Pitches Derived from the Distillation of Fatty Substances.

'Stearine' and 'palm pitches.' Several pitches of this character are met with in commerce, notably those known as 'stearine or cotton oil,' 'wool oil,' and 'palm pitch'; the two first-named representing residues from substances consisting mainly of stearic, the third of palmitic acid. Their manner of preparation is as follows:—

In the purification of crude cotton-seed oil by caustic soda a more or less viscid residue is obtained, known as 'foots' or 'mucilage,' which consists largely of stearic acid in the form of an imperfectly-formed soap. This material constitutes an article well known in Hull, Liverpool, London, and other centres of cotton-oil refining, which has been extensively dealt with for the recovery of stearine and pitch. The soapy mucilage thus obtained in the first instance is heated in suitable vessels, and then gradually decomposed by the addition of dilute sulphuric acid; this treatment separates the 'fatty acids' or 'stearine' in the form of a perfectly-black greasy substance, technically known as 'black grease,' which may vary in quantity from a few p.c. to 80 p.c.

The recovery of stearine and stearine pitch follows as the second step in the operation, and consists in submitting the 'black grease' so obtained to a process of distillation by the aid of superheated steam.

From a 10-ton charge of this material, and at one works known to the writer, the following products are obtained:—

Inferior oils . .	0	12	= 6 p.c.
Stearine . .	3	18	= 39 ,,
Pitch . .	5	0	50 ,,
Loss . . .	0	10	= 5 ,,
Total . .	10	0	= 100 ,,

The pitch thus obtained, and constituting the larger portion of the operation, may be 'hard' or 'soft,' varying with the point to which distillation has been carried. Both are produced and met with in commerce as meeting the requirements of their respective consumers, and present the following characters:—

Soft stearine pitch, a viscid treacly substance, and **Hard stearine pitch**, a firm bright black product, breaking with a well-marked conchoidal fracture. The sp.gr. of this pitch is about 1·35. At 55°C. it softens sufficiently to twist in the manner referred to with coal-tar pitch, and at 95–100°C. it melts. It is almost completely soluble in benzene and the pyridine bases, but to a much lesser degree in petroleum spirit. To this solvent stearine pitch only gives up about 71 p.c. of its organic matter, 23 p.c. remaining insoluble; sulphur is present to the extent of 0·04–0·06 p.c. It yields 79 p.c. of volatile organic matter and 21 p.c. of coke, containing 5 to 6 p.c. of mineral matter or ash. During the operation of heating and burning off a strong, fatty odour is evolved, which at once indicates its origin and nature as an 'oil pitch.'

A benzene solution exhibits no bloom or fluorescence, and when examined spectroscopically a cutting out of the blue and violet portions of the spectrum only; no absorption bands are visible. Stearine pitch has been extensively used for the preparation of special black varnishes used in coating tarpaulins, and in various compounds employed for electrical insulation. For these requirements it is eminently adapted from the fact of yielding surfaces and combinations both supple and pliant, and they do not crack or disintegrate in the manner of some mineral pitches. This pitch, although possessing the excellent qualities referred to, fails to find a ready market at the present time. Oil pitches from other sources have added to the quantity produced, which is now largely in excess of demand.

Wool-oil pitch. In the scouring and washing of woollen goods soapy liquors are obtained in considerable quantity. These liquors are now treated for the fatty substances contained in them. The process followed is in many ways analogous to that already described, the fatty acids being separated by heating and addition of dilute sulphuric acid. On submitting these fatty acids to a similar process of distillation an excellent stearine is recovered, with a similar residue of pitch. This pitch may be hard or soft, and in both stages resembles that known as cotton, or stearine, pitch; it has similar uses and applications. The softer kinds are used as lubricants for heavy machinery, under the name of 'hot and cold neck grease.'

Palm-oil pitch. This pitch, which is now produced in considerable quantity, is the residue of an operation extensively carried out, more or less in accordance with an important patent granted to Wilson and Gwynne in the year 1843, in which oils or other fatty substances were heated with sulphuric acid in place of an alkali for separation of their contained fatty acids. In the operation claimed the glycerine is converted into 'sulphoglyceric acid,' which is afterwards washed out, and the resultant black mass distilled with superheated steam, in each case varying with the fat employed. The respective fatty acids pass over in a condition of great purity and suitability for the various purposes applied. With palm oil, palmitic acid distils over, and palm pitch remains in the still.

In appearance and when soft, this pitch varies from those already described. It is dull in colour, with a waxy feel, but when 'hard' tolerably bright and black in colour, breaking with a distinct conchoidal fracture and small granular surface, but exhibiting the same waxy feel; its sp.gr. varies from 1·045–1·050. The softer kind twists at the ordinary temperature; the harder at 30°C., although it does not completely melt under 95°C. It yields about 80 p.c. of volatile organic matter, and 20 p.c. of a light porous coke, containing 6·5–6·8 p.c. of ash. During heating a powerful fatty odour is given off, betraying its nature as also of fatty origin. It is almost wholly soluble in benzene, but scarcely acted upon by the pyridine bases or petroleum spirit. A solution examined spectroscopically shows a cutting out of the violet portions of the spectrum, but no absorption bands.

Palm pitch has been extensively used for tarpaulin varnishes, and, in combination with paraffin wax, for various electrical insulators. The softer kinds are employed as hot and cold neck greases for heavy machinery.

Bone-oil pitch. In the dry distillation of bones and other animal substances an oil is obtained exhibiting a strong fœtid odour, and known as 'bone' or 'Dippel's oil' (*oleum animale Dippelii*), and when submitted to further distillation yields a hard, firm pitch; from a charge of 3,410 gallons of oil, pitch to the extent of 3½ tons is obtained, representing about 23 p.c.

Hard and soft varieties are produced, and present the following characteristics: Jet black, and shining; brittle, and breaking in masses, although distinctly conchoidal; sp.gr. ranges from 1·125 to 1·130. The harder pitches 'twist' at a temperature of 70°C., and melt at 98 to 100°C. A good sample will yield 63 p.c. of volatile organic matter, and 37 p.c. of hard, compact coke, containing from 0·4 to 0·7 p.c. of mineral matter or ash. During the operation of heating and igniting, the characteristic and unmistakable odour of bone or animal oil becomes very powerful, and readily distinguishes it from all other pitches. As a solvent, benzene attacks it very imperfectly; but the pyridine bases dissolve it entirely, or with the exception of a small quantity of carbonaceous matter. Petroleum spirit dissolves about 30 p.c., leaving 70 p.c. insoluble. Solutions of this pitch in the pyridine bases exhibit no bloom or fluorescence, and when examined spectroscopically merely a cutting out of the violet portion of the spectrum, no absorption bands being visible. Sulphur is present to the extent of 0·30 p.c.

It exhales a somewhat disagreeable odour, very noticeable when warmed; its chief uses are for tarpaulin and other varnishes.

Stockholm pitch (*wood-tar pitch*). Wood tar, when submitted to distillation, yields distillates of light oils varying in sp.gr. from ·840 to ·880. A charge of Stockholm tar, consisting of 2,240 lbs., yields about 14 cwt. of pitch. In appearance it is jet black and brilliant, but inferior to bone pitch. Its fracture is conchoidal, but it is extremely brittle, crumbling between the fingers. It is slightly adhesive, and becomes sticky on gently warming. It has a sp.gr. of about 1·105; at 40°C. it twists easily, and at 82°C. melts. When heated and ignited it yields 88 to 88·5 p.c. of volatile matter, leaving a soft, friable coke ranging from 12 to 11·5 p.c., and containing from 0·7 to 0·84 mineral matter or ash. During the burning off, vapours and odours are evolved impossible to mistake for those of any other pitch, or for other than that of wood tar. Benzene dissolves this pitch completely, and the pyridine bases equally well; but petroleum spirit only takes up from 91 to 92 p.c., leaving a small portion insoluble. Sulphur is present, but in minute quantity only, not exceeding 0·01 p.c.

A solution of Stockholm pitch shows no bloom or fluorescence, and when examined spectroscopically a cutting out of the violet portion of the spectrum only; no bands are visible, nor is there any indication of chrysene, said to exist in this particular tar or pitch.

Stockholm pitch dissolves almost completely in alcohol and potash ley. When its alkaline solution is boiled a coloured oil passes over possessing a stupefying smell, and when acidified and boiled yields volatile fatty acids. A black mass is deposited as the operation proceeds; on boiling this mass with water, creosote is given off. If the acid and alkaline treatment is continued several times, this mass is converted into a black powder, which, after long boiling with hydrochloric acid, yields to alcohol only a small quantity of rosin. The black residue insoluble in alcohol and potash consists of

Carbon	65·04
Hydrogen	4·89
Oxygen	30·07
	100·00

As wood tar is a complex mixture of phenoloid bodies, amongst which guaiacol and creosol predominate, and the less volatile fractions contain methylic ethers of pyrogallol and its homologues, it is highly probable that the residual pitch resulting from its distillation at a comparatively low temperature contains amongst its constituents the methylic ethers of trihydric phenols (*v.* CREOSOTE).

Wood-tar pitch is assumed to possess much of the antiseptic and preservative power of the tar from which it is derived. It finds a considerable outlet for many marine purposes, and the coating and pitching of ships.

Rosin pitch. Rosin, or colophony, is the residue left on distilling off the volatile oils from crude turpentine, and, when submitted to further distillation, yields definite products, but varying considerably with the temperature and conditions of distillation. In a vacuum or current of superheated steam it may be distilled almost unaltered, but when subjected to dry distillation, as in the ordinary method pursued by rosin distillers, it yields a number of products, consisting chiefly of rosin oil, which passes over to the extent of about 85 p.c., including rosin spirit, water, a powerfully anæsthetic gas containing carbonic oxide, ethylene, butylene, and pentene, with a residue of pitch amounting to $1\frac{1}{2}$ cwts. from a ton of rosin. Rosin pitch is a yellowish-brown brittle substance, hard and compact, but easily crumbling on slight pressure; it has a sticky, adhesive feel, and when warmed exhibits the characteristic odour of resin. Its sp.gr. varies from 1·090 to 1·095; at a temperature of 35°C. it twists readily, and at 68°C. melts. When heated and ignited it yields 82·5 p.c. of volatile matter, leaving a spongy soft coke amounting to 17·5 p.c., which contains 0·58 to 0·7 of mineral or ash; during the heating a strong odour of rosin is given off, readily distinguishing it from Stockholm or wood-tar pitch. In benzene and the pyridine bases it is completely soluble, but petroleum spirit only takes up 86·94 p.c., leaving 12·48 p.c. insoluble; sulphur is present to the extent of 0·26 to 0·3 p.c.

Solutions of rosin-pitch exhibit a deep greenish bloom or fluorescence, but differing from that of coal-tar pitch, which is invariably yellow. Spectroscopically, they merely show a cutting or shading-out of the blue and violet portions of the spectrum; absorption bands are absent.

Rosin pitch finds no special use in itself, but is occasionally mixed with other pitches of an inferior description.

Pitches derived from the distillation of petroleum and allied substances. Of these products ozokerite pitch occupies the most important position. It is obtained from the distillation of crude ozokerite, and the following figures have been furnished by E. J. Mills as representative of the operation:

Very light oils	20
Heavy oils	50
Paraffin	8
Hard pitch	8
Loss	14
	100

B. Redwood (Jour. Soc. Arts, xxxiv. 886) gives the products of Galician ozokerite as 5 p.c. of gaseous hydrocarbons, 3 p.c. of naphtha, 6 p.c. of semi-solid 'ozokerine,' 12 p.c. of soft paraffin melting at 44 to 46 C., distilled ozokerite [illegible] at 64 C., [illegible] black, waxy [illegible]. A sample of the pitch supplied by Messrs. Field & Co., of Lambeth, and examined by the writer, consisted of a hard waxy substance breaking with rough granular surface, and metallic lustre. Its colour [illegible], inclining to brown. Its sp.gr. was 0·950. At a temperature of 50 C. it 'twisted' and at 85 C. melted; heated and ignited it yielded 97 p.c. of volatile organic matter, leaving 3 p.c. of a soft, friable coke, containing traces only of mineral matter or ash. During this operation the odour evolved was simply that of highly-heated paraffin. It was completely soluble in benzene, but not wholly so in the pyridine bases, the solution showing no bloom or fluorescence; examined spectroscopically, no absorption bands were visible, but a cutting-out of the blue and violet portions of the spectrum only, as in the case of the pitches already described.

Ozokerite and ozokerite pitch have been found to possess remarkable electrical qualities, and in admixture with various substances, caoutchouc amongst them, have formed the subject-matter of several patents. Such compounds have found extensive uses for coating telegraphic wires, and for insulating purposes generally.

Petroleum pitch. In the first distillation of crude petroleum oil, the charges may be run down to a coking-point, or they may be discontinued at a stage at which a pitch or artificial asphaltum would result on cooling.

In appearance it greatly resembles natural bitumen or asphaltum; it is jet black and shining, and breaks with a similar conchoidal fracture. It has a sp.gr. of about 1·120; at a temperature of 45 C. it 'twists,' and at 84° to 85 C. melts; heated and finally ignited it yields about half its weight of volatile organic matter. The odour evolved is characteristic of petroleum, but differs entirely from that of natural asphaltums, with which it cannot be confounded. Mineral matter is present in minute traces only. Benzene dissolves this pitch completely, affording a solution exhibiting a strong yellow bloom or fluorescence not unlike that observed with coal-tar pitch. It is, however, almost insoluble in the pyridine bases; petroleum spirit dissolves 36·16 p.c. only. The residues from American petroleum contain notable quantities of close chain hydrocarbons, among which anthracene, phenanthrene, chrysene, chrysogene, and pyrene have been recognised, as also a hydrocarbon called thallene; from Californian petroleum the hydrocarbon picene ($C_{22}H_{14}$) has been isolated. When treated with sulphuric acid, it yields a sulphonic acid dissolving in water with a splendid blue-green fluorescence. Petroleum pitch, although differing in its physical aspect, may in many respects be looked upon as re-[illegible].

B. Poro (Gazzetta 13, 77–85) gives the following figures as showing results of distilling Italian petroleum:

	I.	II.
Oil	63·5	66·9
Pitch	32·2	28·3

Petroleum pitch has been used in compounding cements, asphalts, varnishes and patent fuels, but as an article of commerce it has no present demand in England.

Shale oil pitch is now quite unknown, manufacturers of shale oil preferring to continue its distillation to the extent of 'coking.'

Bibliography.—Lunge's Coal Tar and Ammonia (2nd edit.), 1887; Allen's Commercial Organic Analysis (2nd edit.), 1886; E. J. Mills, Destructive Distillation; Watts' Dictionary of Chemistry; S. F. Peckham (Am. S. [3] 28, 105–117); Stripplemann and Engler (D. P. J. 250, 216, 227, 265, 271, 316, 321); Boussingault (C. R. 96, 1452, 1456); B. Delachanal (C. R. 97, 491, 494). B. N.

PITCHBLENDE *v.* URANIUM.

PITTACAL *v.* WOOD, DISTILLATION OF.

PLASTER OF PARIS *v.* CALCIUM; also CEMENTS.

PLASTIC CLAY *v.* CLAY.

PLATINOTYPE PROCESS *v.* PHOTOGRAPHY.

PLATINUM METALS. Under this heading are included platinum, palladium, iridium, osmium, rhodium, and ruthenium. These metals are found in the mineral known as *Native platinum*, which occurs, usually, in alluvial deposits from the older volcanic formations.

Native platinum is found in the Ural mountains; in the washings from the river Pinto, in Brazil; in Choco, New Granada; in the Natoos mountains of Borneo; in California, Mexico, Australia; in the nickeliferous ores of Sudbury, Canada, and many other localities. These metals are occasionally present in very small quantities in many common minerals, as in *dolomite*, *barytes*, and the ores of *lead* and of *silver*.

The ore consists principally of rounded or flattened grains of metallic lustre, occasionally in cubes or octahedra, more rarely in nuggets. Mixed with these grains, which consist of platinum alloyed with smaller quantities of associated metals, are a number of small flat grains or hexagonal prisms of *osmiridium*, otherwise known as *iridosmine* or *native iridium*, consisting of an alloy of *iridium* and *osmium*, always containing *rhodium* and *ruthenium*, and usually varying proportions of *platinum*, &c. Small rounded cubes or grains of *platin-iridium*, an alloy of those two metals, are also found.

The following analyses show the composition of these minerals:—

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Iron	[illegible]	[illegible]	[illegible]	[illegible]
1. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	100·25
2. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	101·15
3. [illegible]	[illegible]	[illegible]	[illegible]	1·35	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4. Australia . .	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1·20	—	[illegible]
5. Urals . .	[illegible]	[illegible]	[illegible]	1·10	[illegible]	4·10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6. [illegible] . .	[illegible]	[illegible]	[illegible]	1·10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
7. Borneo . . .	[illegible]	[illegible]	[illegible]	[illegible]	—	0·34	[illegible]	—	[illegible]	[illegible]	—

—	Iridium	Osmium	Platinum	Rhodium	Ruthenium	Palladium	Iron	Copper	Total
Platin-iridium									
1. Urals . .	76·85	—	19·64	—	—	0·89	—	1·78	99·16
2. Brazil . .	27·79	—	55·44	6·86	—	—	4·14	3·30	98·02
Osmiridium									
3. Urals . .	55·24	27·23	10·08	1·51	5·85	tr.	tr.	tr.	100·00
4. New Granada .	27·80	31·10	—	0·63	6·37	—	0·10	0·06	100·06
5. California .	53·50	43·40	—	2·60	0·50	—	—	—	100·00
6. Australia. .	58·13	33·46	—	3·04	5·22	—	—	0·15	100·00

Nos. 1–5 are by Deville and Debray (A. Ch. [3] 56, 449), No. 6 by Le Play, No. 7 by Bleekerode (P. 103, 656). The second table is taken from Roscoe and Schorlemmer's Manual II. (2) 438. Compare Wilm. B. 18, 2,536.

An account of the Russian auriferous sands in which the platinum ore occurs is given in 'Engineering,' 31, 163.

The ore is separated in the same manner as gold from the admixed sand. Each pound of ore is produced by the washing of nearly 54 tons of sand.

The production of platinum ore in Russia within recent years is as follows:—

In 1881, 2,986 kilos. were produced; in 1882, 4,081 kilos.; in 1883, 3,537 kilos.; in 1884, 2,237 kilos.; in 1885, 2,591 kilos.; and in 1886, 4,317 kilos., or an average of hardly 660 cwt. a year. All this platinum is found in two districts of the Government of Perm. The mines of Goroblagodsk yield about two-thirds, those of Nijni-Tagilsk one-third, of the supply. In the Ural mines, until some years ago, platinum was obtained as a kind of by-product in the working of the auriferous deposits, the existence of which led to the opening of these mines. But during the last few years the gold ore has become much scarcer, and platinum has superseded gold as the principal product of the mines. The recent advance in the price of the metal is attributed partly to the increasing scarcity of the ore, and partly to the fact that labour, always an uncertain factor in the Ural mines, has become excessively scarce since the commencement of the Trans-Siberian railway. According to later advices, the whole of the platinum which will be produced in the Ural mines for the next ten years has been sold in advance to certain foreign companies. Owing to these contracts the price of platinum has advanced from 2,500 to 12,500 roubles per pood.

Platinum. Symbol Pt. At. wt. 194·3 (Berzelius, Seubert, Halberstadt).

The development of the metallurgy of platinum, and the introduction of the metal for commercial uses, originated in England, and is entirely due to the firm of Johnson, Matthey, & Co., who worked platinum for many years before any other commercial manufactory was established.

Between the years 1800 and 1808, Mr. Thomas Cock, a relative of the late Mr. Percival Norton Johnson, a grandson of the original founder of the firm, was occupied in working upon platinum, and discovered the process for its treatment and consolidation, which, usually known as the process of Wollaston, has been, until comparatively late years, the only known process.

Mr. Percival N. Johnson, F.R.S., with the skill and energy which made his name famous in the first half of this century as a metallurgical chemist, commenced the refining and working of platinum in Hatton Garden immediately after Mr. Cock's discovery.

Mr. Cock's original process is as follows: The ore is digested in a retort containing slightly-diluted hydrochloric acid, nitric acid being added in successive small portions. The hydrochloric acid having become nearly saturated, the solution is evaporated to a syrup, to remove the excess of acid, diluted, and decanted from the insoluble portion. The residue may be treated a second time to completely exhaust it. The portion still insoluble contains osmiridium, sand, chrome iron ore, spinelle, &c.

To the red solution, which contains platinum, with small quantities of all the platinum metals, is added a solution of ammonium chloride in 5 parts of water (41 parts of the chloride to 100 parts of ore), when the platinum is precipitated as the sparingly-soluble double chloride of ammonium and platinum, together with a small proportion of the corresponding iridium compound. The mother-liquor, which still contains platinum with the associated metals, is treated with metallic iron, and the precipitated metals are digested in hydrochloric acid to remove iron, dissolved in aqua regia, precipitated as before, and the precipitate added to the former. The mother-liquor contains nearly the whole of the rhodium, ruthenium, palladium, and a little of the osmium, originally present in the portions of ore soluble in aqua regia.

The washed precipitate is heated to dull redness to drive off the ammonium chloride and chlorine, leaving *spongy platinum* in a slightly coherent form. This is rubbed to a powder with the hands and passed through a linen bag, the harder portions being powdered in a wooden mortar. The powder is elutriated, and the finer powder thus separated is made into a paste with water and placed in a brass cylinder previously filled with water, sufficient being added to fill the cylinder and replace the water. In this way all cavities are avoided. The metal is then strongly compressed, and the solid metallic-looking cake produced is heated to redness to drive off all the water and render it more coherent, and exposed for twenty minutes to intense heat in a blast furnace. The cake, while still red hot, is placed on an anvil and repeatedly hammered on its ends with a heavy hammer. The metal has then a density of about 21·25, and may be worked into any desired form by heat and hammering. Unless again refined, which makes it practically pure, it always contains about 2 p.c. iridium (which is advantageous for certain purposes), and traces of osmium and other metals and of silicon.

According to J. Phillip (Hoffmann's Ber. Entr. Chem. Ind. [1] 999) the following modification is adopted by Heraeus of Hanau: The raw ore is treated in glass retorts, under a pressure of 12 inches of water, with aqua regia, diluted with two parts of water, the solution evaporated to dryness and heated to 125° C., to reduce the rhodium and palladium to lower chlorides, and the residue is digested with water.

The clear, decanted solution is acidulated with hydrochloric acid, and precipitated with ammonium chloride. The mother-liquor is precipitated with iron and treated as before described. The double chloride is ignited, compressed, broken to pieces, and fused by means of the oxyhydrogen blowpipe in a lime crucible.

Deville and Debray (A. Ch. [3] 56, 419) have proposed a process for the preparation of platinum directly from the ore. A small reverberatory furnace having a hemispherical bed of fire-brick, lined with clay, is heated to full redness, and a charge of about 2 cwts. of ore, mixed with an equal weight of galena, is added in small charges with frequent stirring. A small quantity of glass is then added to form a fusible flux with the lead, and about 2 cwts. of litharge is thrown in in successive portions. The sulphur is thus oxidised and expelled, while the liberated lead forms a fusible alloy with the platinum, beneath which the unattacked osmiridium gradually sinks.

The upper portions are removed by iron ladles, and the remaining portions, containing the osmiridium, are added to a subsequent fusion. The alloy is cupelled, and the whole of the lead removed, together with most of the injurious impurities, leaving very malleable, nearly pure platinum. The metal is purified by fusion under the oxyhydrogen blow-pipe.

They also recommend the fusion of the ore with a quantity of admixed lime equal to the amount of iron present. The fusion is performed in a lime crucible by the oxyhydrogen blow-pipe. Copper and iron are thus oxidised and pass into the lime, while palladium and osmium are volatilised. The metal produced contains iridium and rhodium, and is very suitable for making vessels for chemical purposes, as it is more refractory and less acted upon by reagents than pure platinum.

The fusion of platinum on an industrial scale was first effected by H. St.-Claire Deville and Debray about the year 1856, and the process was immediately adopted by Johnson, Matthey, & Co. By the fusion of pure sponge-platinum (instead of its simple compression by forging under the old system) it is obtained in a condition of the most perfect compactness, strength, and durability, and of increased resistance to the action of acid. In the year of the International Exhibition, 1862, Johnson, Matthey, & Co. melted, in the presence of many of the principal *savants* of Europe, 3,250 ounces of this metal, and the single ingot which was the result of the fusion formed one of the objects of attraction in their exhibit at the exhibition.

Deville and Debray's method is as follows:—The metal, after compression, is placed in a hollow in the lower of two well-fitting pieces of lime, through an opening in the upper of which passes the nozzle of an oxyhydrogen blow-pipe. The metal is fused in the blast, the products of combustion passing through an opening in the sides of the two pieces of lime, which also serves as an outlet for the molten metal; the osmium is volatilised as the tetroxide, while the silicon, in the form of calcium silicate, and the iron and copper as oxides, are absorbed by the lime.

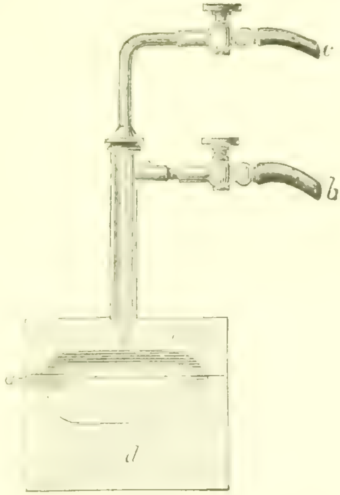

FIG. 1.

For the preparation of pure platinum the following process is adopted by G. Matthey (Pr. 28, 463; C. N. 39, 175). Commercial platinum is melted with 6 parts of *pure* lead, and the alloy is granulated by pouring into water, and dissolved in a mixture of 1 part nitric acid and 8 parts distilled water, a fresh portion of the solvent being added as it becomes saturated.

In this manner most of the lead is dissolved, with a portion of the copper, iron, palladium, and rhodium; the lead nitrate may be separated by crystallisation, while the other metals may be precipitated as usual.

The black amorphous residue left by the nitric acid contains lead, platinum, and iridium, in brilliant crystals, together with other metals. It is digested in weak aqua regia, which removes the lead and platinum, leaving iridium, ruthenium, and iron, but separating the whole of the platinum. The solution is evaporated, and treated with just sufficient sulphuric acid to precipitate the whole of the lead; the platinum chloride is dissolved in distilled water, treated with excess of ammonium and sodium chloride in order to precipitate the double chloride in a saturated solution of the precipitant, heated to about 80° C., and allowed to settle for a few days. The platinum-ammonium chloride is deposited, the liquid above being usually rose-tinted from the presence of *rhodium*. The precipitate is washed repeatedly with a saturated ammonium chloride solution, and finally with water acidulated with hydrochloric acid. The washings may be treated to recover the dissolved platinum.

The dried precipitate, which may still contain rhodium, is mixed with potassium bisulphate and ammonium bisulphate, and gradually heated in a platinum capsule, covered by an inverted glass funnel, to dull redness. The platinum is thus reduced to black, spongy, porous metal, while the rhodium remains as soluble bisulphate of rhodium and potassium, and is dissolved out by water. The liquid is again evaporated, and heated to redness as before to reduce the small portion of platinum previously dissolved.

The metal so obtained has a density of 21·46, which is stated by Matthey to be the highest obtainable.

A similar but less complete process is described by Deville and Debray (C. R. 81, 839).

Properties.—Platinum is a tin-white metal nearly as hard as copper. When alloyed with iridium it is harder than the pure metal. In malleability it ranks next to gold and silver. It is ductile and easily polished. It may be drawn into fine wire through steel plates. Wires have thus been made $\frac{1}{1200}$th of an inch in diameter, and by coating a thin wire with silver, drawing the compound wire to great fineness and removing the surrounding silver by nitric acid, a wire of platinum has been produced only $\frac{1}{30000}$th of an inch in diameter.

Its specific gravity is 21·46 (G. Matthey), 21·48 to 21·50 (Deville and Debray). Platinum has been obtained in minute crystals by heating platinum tetrafluoride (Moissan). Joly has also obtained the metal in forms derived from the regular system by strongly heating it with finely-powdered topaz or quartz dust. Platinum tetrafluoride is probably formed in the first case, and is subsequently decomposed. Similar crystals have been formed by Törnebohm, by strongly heating platinum black in chlorine gas.

Platinum welds at a red heat, and fuses under the oxyhydrogen blow-pipe at 2000°C. (Deville), 1750° (Violle), absorbing oxygen, and 'spitting' like silver when cooled in large masses. By means of the oxyhydrogen blow-pipe it may be soldered very perfectly with itself.

The autogenous soldering of platinum (*i.e.* the joining together of platinum by means of the oxyhydrogen blow-pipe) was a very great advance in the manufacture of platinum, and this process was perfected by Johnson, Matthey, & Co. in the year 1860, and has been adopted ever since. The platinum vessels exhibited by them in the London Exhibition of 1862 were all manufactured upon this system.

Its expansion by heat is about equal to that of ordinary glass, and is less than that of any other metal. This property is of great importance, as platinum wires, &c., can be fused in glass tubes without danger of cracking under variations of temperature. Its thermal and electric conductivities are low. At a strong red heat, platinum is permeable to hydrogen (*v.* Palladium). It absorbs, at a red heat, 3·8 volumes of hydrogen, which are again evolved on heating *in vacuo*.

It condenses oxygen, apparently, on its surface. On this account, a spiral of platinum wire, when placed in a mixture of oxygen and hydrogen or other inflammable gas, by bringing them into intimate contact induces their combination, becoming itself heated to redness, and sometimes igniting the mixture. This is well seen by suspending a platinum spiral over a small quantity of alcohol or ether in an open flask. The oxidising power is possessed in a much greater degree by *platinum black* or *spongy platinum*, on account of their extended surface.

Spongy platinum is prepared by ignition of the ammonium platinum chloride. It forms a porous mass, which may be polished by a burnisher, and becomes denser on ignition.

Platinum black may be prepared by warming a solution of platinous chloride in potash with alcohol, as a residue from the treatment of alloys of platinum and other metals by nitric acid, and by precipitating platinum from dilute solutions by other metals or by reducing agents. A very active form is produced by adding a solution of platinum tetrachloride to a boiling mixture of 3 parts glycerine and 2 parts caustic potash solution (density 1·08) (Zdrawkowitch, Bl. [2] 25, 198). According to Liebig, it absorbs 800 volumes of oxygen. After frequent ignition it becomes denser and less active. It is a powerful oxidising agent, and is frequently used on that account in organic chemistry.

Endeavours have been made to use platinum black on the large scale for the preparation of pure acetic acid from alcohol (*v.* Acetic acid).

Platinum is not attacked by oxygen, water, or nitric acid. At a high degree of concentration, *pure* boiling sulphuric acid will dissolve platinum. According to Scheurer-Kestner (C. R. 91, 59) the action of chamber acid on platinum stills is due to the presence of a *minute* quantity of the oxides of nitrogen. The action, if due to oxides of nitrogen, might be prevented by the addition of ammonium sulphate, which decomposes these oxides.

Platinum is oxidised by fused alkalis in presence of air, especially by lithia or baryta. The action appears to be due to the production of a small quantity of a powerfully-oxidising alkaline peroxide; it does not take place in an atmosphere of hydrogen. *Potassium nitrate* also oxidises platinum.

Platinum, especially in the spongy form, is dissolved by boiling concentrated solutions of alkaline cyanides with evolution of hydrogen and formation of double cyanide of platinum and alkali (Deville and Debray, C. R. 82, 241).

An alloy of platinum with 10 parts of silver is wholly soluble in nitric acid.

Great care is necessary in the use of platinum vessels. Silica, in presence of carbon, attacks platinum; these crucibles should therefore never be heated in contact with solid fuel. According to Ruchardt (D. P. J. 240, 216), the presence of 0·001 p.c. of silicon renders platinum brittle.

Smoky flames or flames free from smoke, where combustion is not complete, attack platinum, forming a carbide which is re-oxidised in the oxidising portions of the flame into a detached, greyish, surface coating, which would soon penetrate the whole crucible, and render it brittle and useless. Crucibles should be rubbed until polished with a little moistened sand whenever this appearance is seen. They then become again malleable with very slight loss of weight.

Compounds of reducible metals, such as silver, tin, lead, arsenic, and many others, should not be heated in platinum crucibles, as, under the action of reducing gases, &c., they form very fusible alloys and destroy the vessel. Compounds of phosphorus have the same property. Phosphorus, indeed, combines so readily that alloys are formed at a very low temperature.

A little potassium bisulphate fused in a platinum vessel will cleanse its surface, especially from iron. A good platinum vessel should lose no weight on digestion in boiling nitric acid or in boiling hydrochloric acid (free from chlorine).

Notwithstanding its high price, platinum is used, on account of its permanence, for the manufacture of sulphuric acid stills, &c.

The first apparatus of platinum ever made for the concentration of sulphuric acid was completed in December 1809, and was supplied to some works now existing near London. The weight of platinum used in this piece of apparatus was 423 ounces troy; it was of a deep circular form, and up to about 1855 similar vessels, either entirely of platinum or fitted with leaden hoods, were used, the principle being the digestion of a deep layer of acid for a considerable time.

In the Paris Exhibition of 1855, Johnson, Matthey, & Co. exhibited a *gold-lined* still, which rendered it possible to run through in a continuous stream a shallow layer of acid, a principle now universally adopted in the rectification of sulphuric acid. Since that date, under the supervision of Mr. John S. Sellon, the nephew of the late P. N. Johnson, several hundred stills of perfected forms, of a value of from 1,000*l.* to 8,000*l.* each, have been sent to various parts of the world, as much as 40,000 ounces of platinum, representing a present value of 100,000*l.*, having been worked up for this purpose alone in a single year.

It is said that *clean* brass, tin, copper, &c., may be coated with platinum, by rubbing on a solution of 1 part platinum tetrachloride dissolved in 15 parts of alcohol and 50 parts ether. The surface is dried and polished with a dry cotton or woollen cloth. The coating is permanent, and resembles polished steel (C. C. 1882, 384).

Platinum when alloyed with other metals, such as zinc, tin, and lead, or in contact with them, increases their solubility by setting up a voltaic action.

The presence of thallium has been observed in platinum ores and in the worked metal (H. N. Warren, C. N. 55, 241).

Detection.—Compounds of platinum are decomposed, with separation of platinum on ignition.

Sulphuretted hydrogen and ammonium sulphide precipitate platinum from solutions as sulphide; it is soluble in excess of alkaline sulphide, and is re-precipitated by hydrochloric acid.

The chloride gives, with potassium or ammonium chloride, the well-known yellow precipitates. Platinum salts are reduced to the metallic state by mercurous nitrate, but not by ferrous sulphate or oxalic acid.

Estimation.—Platinum is always weighed as metal. The metal, in concentrated solution as chloride, is treated with a strong solution of ammonium or potassium chloride, evaporated until it becomes pasty, treated with alcohol, and the precipitate filtered off, and washed with alcohol. The precipitate is ignited and weighed as metal when ammonium chloride is used as precipitant, or, when potassium chloride is employed, the ignited mass is washed with water to remove potassium chloride, filtered, dried, ignited, and weighed. This metal would also contain iridium and small quantities of the other platinum metals if present in the solution.

Lengthy methods for the separation of the metals in platinum ores and residues are given by Deville and Debray (A. Ch. [3] 56, 439, and 463) and by Claus (Beiträge zur Geschichte der Platinmetalle).

ALLOYS.

The alloys of platinum, especially that of 10 p.c. iridium, have become of great importance in the arts, and have been of much service to science.

The alloys with *iridium* are given under that metal. The alloy of 30 p.c. *rhodium*, 70 p.c. platinum is unacted upon by aqua regia (Deville).

An alloy of equal parts of *palladium* and platinum is grey, as hard as iron, and melts below the melting-point of palladium.

An alloy of three parts *gold* and seven parts platinum is infusible in a strong blast furnace. An increase of gold increases the fusibility. With two parts platinum and one part gold the alloy is brittle; with equal parts it is malleable and nearly the colour of gold; the alloy containing nine parts gold and one part platinum is very elastic.

Mr. Edward Matthey has shown (Pr. 47, 1890, p. 180) that when platinum-gold alloys are cast into moulds the platinum becomes concentrated towards the centre of the mass, a point of much interest in connection with the liquation of alloys. This fact explains the difficulty which has been met with in determining the value of ingots of platiniferous gold on the result of assay pieces cut from the exterior of ingots.

Silver alloys in all proportions with platinum. The presence of a small quantity of platinum renders silver hard. Hot sulphuric acid removes the silver from these alloys. Nitric acid removes the silver and a portion of the platinum; when the proportion of the latter is less than 10 p.c. the whole is dissolved. An alloy of three parts silver, one part copper, and four parts platinum, is said to be used for metallic pens (Busch, D. P. G. 240, 216).

With *antimony*, platinum unites with incandescence, fusing on further heating to a steel-grey brittle alloy. With excess of *arsenic* an alloy is produced with incandescence, which is brittle and easily fusible. When heated below the melting-point, the arsenic is gradually volatilised, leaving porous platinum in the shape previously occupied by the alloy, and in a fit state for working. This alloy, first used by Achard in 1784, was employed for a considerable time as the only means of working platinum.

Bismuth two parts, and spongy platinum one part, combine readily, forming a bluish-grey, brittle, fusible, laminated alloy. When fused at a moderate heat, the metals partially separate.

On heating with *cadmium* and driving off the excess by heat, platinum forms a silver-white, refractory, brittle, fine-grained alloy, corresponding nearly to $PtCd_2$. With *copper* combination ensues at a white heat. All the alloys take a good polish. That consisting of equal parts, fused in the oxyhydrogen blowpipe, is yellow and easily tarnished. An alloy of 26 parts copper and 1 part platinum is malleable, rose-coloured, and of fine grain.

Lead combines easily with platinum. The alloy produced by heating to redness one part platinum with 2·7 parts lead, is easily fusible, fibrous, and brittle ; with two parts of lead it is rather more brittle; with equal parts it is striated, hard, brittle, and granular. These alloys lose nearly all their lead on cupellation, about 2 p.c. being retained.

When strongly heated with one part of *nickel*, a pale yellowish-white, malleable, magnetic alloy is formed, which takes a high polish and is as fusible as copper. With an equal weight of *tin* the alloy is hard, brittle, rather fusible, and coarse grained. Deville and Debray have obtained alloys corresponding to Pt_2Sn_3 and $PtSn_4$.

Zinc filings heated below the melting-point of zinc with platinum black combine with incandescence.

With *potassium* combination takes place readily, with incandescence, forming a shining brittle alloy, which oxidises in air or water, forming potassium hydrate and leaving black scales of platinum or platinum hydride.

Oxides. Platinum forms two oxides, platinous oxide PtO, and platinic oxide PtO_2. Two series of salts are known, corresponding to these oxides.

Platinic chloride $PtCl_4$ is prepared by dissolving the metal in aqua regia, and evaporating the solution to dryness on the water-bath. It is a deliquescent salt, crystallising in prisms containing ten molecules of water; it is freely soluble in water, alcohol, and ether.

When the aqua regia solution is evaporated with frequent addition of hydrochloric acid as the nitric acid is evolved, the liquid contains *chloroplatinic acid*, $PtCl_42HCl$, which is the salt generally known as platinic chloride. It may be obtained in large brownish-red deliquescent crystals containing six molecules of water. Its hydrochloric acid is readily replaced by metallic chlorides, producing *double chlorides*. The same salts are produced with the normal platinic chloride. Of these, only the three following are of interest:—

Potassium platinic chloride $PtCl_42KCl$ is precipitated in small yellow crystals by the addition of a strong solution of potassium chloride to a strong solution of platinic chloride. From a hot solution it may be crystallised in small reddish-yellow octahedra. 100 parts of water dissolve, at 0°C. 0·7, and at 100°C. 5·18, parts of this salt (Bunsen and Kirchhoff). It is insoluble in a saturated solution of potassium chloride, and in alcohol and ether, soluble in alkaline hydrate, re-precipitated from the solution by acids. On ignition, it is converted into a mixture of *spongy platinum* and potassium chloride, with evolution of chlorine.

Sodium platinic chloride $PtCl_42NaCl$ is prepared similarly to the former salt. It is easily soluble in water and alcohol.

Ammonium platinic chloride $PtCl_42(NH_4)Cl$ is prepared like the potassium salt. Its appearance resembles that of the potassium salt. 100 parts of water dissolve 1·25 parts at 100°C. It is almost insoluble in a saturated ammonium chloride solution, insoluble in alcohol and ether. When ignited it produces pure *spongy platinum*, with evolution of ammonium chloride and chlorine.

Platinous chloride $PtCl_2$ is produced on heating chloroplatinic acid or the normal chloride to 240°C., or by heating spongy platinum in dry chlorine between 240° and 250°C. (Schützenberger, A. Ch. [4] 21, 351). It is a greenish-grey powder, insoluble in water.

Potassium platinous chloride $PtCl_22KCl$ is prepared by the addition of moist cuprous chloride to a thick paste of *potassium platinic chloride*, which is then warmed and stirred until the greater part is dissolved. Sufficient cuprous chloride should not be added to decompose the whole of the platinum salt. The solution is filtered, cooled, and the platinous salt crystallised out. The crystals are washed with alcohol, and on recrystallising from water form soft, rose-coloured fibres (Magnus).

This compound has found an important application in photography in the permanent *platinotype process*. (See Willis, Photog. News, 1878, 397, and other references in that and following volumes). (*V.* PHOTOGRAPHY.)

Palladium. Symbol Pd. At. w. 106·35 (Keiser).

This metal, discovered by Wollaston in 1803, is found in grains, usually containing platinum and iridium, mixed with Brazilian platinum ore. In palladiferous gold it forms 5 or 6 p.c. of the gold washings of Brazil. A sample from Taguaril (Brazil) contained 8·21 p.c. palladium. It occurs with gold and silver to the extent of 10 p.c. at Porpez, in South America. Mixed with gold and lead selenide it is found at Tilkerode, in the Hartz.

A method for separating palladium from auriferous ores is described by Cock (P. M. [3] 23, 16).

Palladium remains in the solution of the platinum ore after the precipitation of platinum. By addition of potassium cyanide to the neutral solution, it may be precipitated as a white flocculent cyanide, yielding palladium on ignition.

An ingot of palladium in the possession of Messrs. Johnson, Matthey, & Co., valued at 2,000*l.* was extracted from one million pounds' worth of platinum ore.

Properties.—Palladium is a white, lustrous metal of sp.gr. 11·4 at 22·5° (Deville and Debray). It is about as hard as platinum, but rather less ductile. Palladium is the most fusible of the platinum metals, melting at the highest heat of a forge (at 1700°C. according to Pictet; 1500°, Violle). It is quite unalterable in air ; at a low red heat it becomes iridescent from superficial oxidation, but is again reduced at a higher temperature. At the melting-point of iridium, it is again partially oxidised, and volatilises in greenish vapours. When melted it absorbs oxygen, and evolves it only on solidification, thus rendering the metal very porous. It dissolves in nitric acid, and is easily soluble in *aqua regia*. The action of concentrated boiling hydrochloric, or sulphuric acid is slight. Tincture of iodine blackens the surface of palladium (distinction from platinum).

Palladium is sometimes used for the divided scales of astronomical instruments, as a superior substitute for silver plating, and as a substitute for gold in tooth stopping. When heated in a spirit-lamp flame it becomes corroded, expanding, and being penetrated by carbon, and covered by a soot containing palladium. It exerts a peculiar action on coal gas. If exposed in a tube or crucible at a red heat to a current of that gas, a considerable quantity of carbon is deposited in cauliflower-like masses near the metal. These are said to contain no palladium, while the palladium contains no carbon (C. C. 1882, 384).

A palladium wire heated to redness in hydrogen absorbs 935 volumes of the gas, and increases in bulk about 9·8 p.c. Even at the ordinary temperatures it absorbs 376 volumes of hydrogen. No change is visible in the metal, but its conductivity for heat and electricity is reduced. It is usually stable, both in the air and *in vacuo*, but the whole of the hydrogen is liberated on heating *in vacuo*. According to Troost and Hautefeuille, it consists of Pd_2H. It is a powerful reducing agent.

At a red heat palladium is easily permeable to hydrogen. A surface of one square mètre allows nearly 4,000 c.c. of hydrogen to pass through per minute, while through *caoutchouc* of the same thickness the permeability is only 127·2, and through *platinum* only 489·2.

The salts of palladium are unimportant. It forms three oxides and two chlorides. The double chlorides corresponding to those of platinum are soluble.

Alloys.—Palladium unites with most metals, but the combinations are unimportant.

Gold containing a very little palladium is brittle. The alloy of equal parts of these metals is coarse-grained, and less ductile than either constituent. With 1 part palladium and 4 parts gold it is white, hard, and ductile; with 1 palladium and 6 gold it is still nearly white.

Palladium black (prepared in the same manner as platinum black) unites with zinc filings with deflagration, when heated below the fusing point of zinc.

Iridium. Symbol Ir. At. w. 192·5 (Seubert).

Iridium occurs in platinum ore, principally as 'osmiridium' and 'platiniridium.' Analyses, &c., have already been given.

Osmiridium, on account of its extreme hardness, its infusibility and indifference to reagents, is used in its native condition for pointing pens, for watch and compass bearings, and for other hard-wearing surfaces. The principal district from which it is obtained is Katharinenberg, which produces about 200 ounces annually. Other districts in the Urals and California come next in order of production. The Californian mineral, being heavier, denser, harder, and containing less platinum than that from Russia, is best suited for general purposes.

One ounce of the mineral contains from 3,000–6,000 grains. Many of these are too small to be of use, and others, on account of their laminated structure, break during working. Only about 10 p.c. are found available for pen points.

A suitable grain is fixed to the end of the pen by ordinary silver solder, cut through to form the two halves of the nib by means of a revolving copper plate tipped with diamond dust, and ground to the required shape on a revolving copper plate with emery and oil. In this way about 30 ounces are used annually in the United States.

The large quantity of waste grains are said to be worked up easily by a process patented by Holland. The ore is heated to redness in a Hessian crucible, and a stick of *phosphorus* is added. In this way the ore is melted, a phosphide of iridium being produced, containing about 7 p.c. of phosphorus and corresponding to PIr_2. It contains a far smaller proportion of *osmium* than the ore, the greater part of that metal being volatilised.

The phosphide is poured, while liquid, between two steel plates and rapidly pressed to the required thickness, usually about $\frac{1}{32}$ of an inch. It is then broken or cut to the required size, and may be used for tipping pens and for a large number of other purposes.

This alloy appears quite metallic, is liquid at a red heat; harder, lighter (sp.gr. 13·77), and less brittle than osmiridium, and takes an equal or superior polish.

The phosphorus may be eliminated, if desired. The phosphide is embedded in lime contained in a Hessian crucible and heated intensely. The metal is cooled, and again treated with a fresh charge of lime for a longer time, until, after four or five ignitions, the whole of the phosphorus is removed, leaving the metal tough, as infusible as ordinary iridium, and slightly porous. Thus treated, it has been used for the negative electrode of the electric light. (See Dudley, Proc. Ohio Mech. Inst. [1] 35; C. N. 45, 168; F. W. Clarke and O. Joslin, Am. 5, 231; and a lengthy article on iridium, including its bibliography, by Perry, C. N. 51, 1, 19, 31.)

The following process may be used for separating crude iridium from osmiridium. Mix the powdered mineral with 1 part of powdered, fused sodium chloride, and heat to dull redness in a tube, in a current of dry chlorine. Iridium and osmium are thus converted into double chlorides with sodium chloride. They are dissolved out by boiling water, concentrated, mixed with nitric acid, and distilled until the whole of the osmium has volatilised as oxide. The residual solution is concentrated, treated with ammonium chloride, and the precipitated iridium ammonium chloride is ignited to *spongy iridium* (Wöhler). Osmiridium may be rendered more readily acted upon by fusing with zinc and a little ammonium chloride. The metals then combine, and the zinc may be dissolved out by dilute sulphuric acid, leaving iridium and osmium as impalpable powders.

The purest commercial iridium contains platinum, rhodium, ruthenium, and iron. G. Matthey (Pr. 28, 466; C. N. 39, 175) adopts the following process for removing all impurities except a small quantity of platinum, which, for purposes for which iridium is usually required, is not injurious. The finely-powdered commercial metal is fused with 10 parts of *pure* lead, and kept in fusion for some hours. The cooled mass is heated with nitric acid to remove lead, and the residue is digested for a considerable time in *aqua regia*, leaving a crystalline mass of iridium, rhodium, ruthenium, and iron. This is fused at a high temperature with potassium bisulphate, cooled, and digested with water. Rhodium is thus removed as the double sulphate of rhodium and potassium, leaving only a trace of that metal, which is removed subsequently, with the iron. The residue is melted for a considerable time with 10 parts dry potash and 3 parts potassium nitrate in a gold crucible. The cooled mass is digested with cold distilled water to remove the potassium rutheniate thus produced, leaving only bluish potassium iridiate mixed with ferric oxide. This residue is well washed with water containing a little potash and sodium hypochlorite until the washings are colourless, and, finally, with distilled water.

The blue residue is mixed with water containing excess of sodium hypochlorite, and digested in the cold for some time, transferred to a distilling vessel, warmed, and finally distilled until the distillate no longer imparts a red tinge to diluted alcohol acidulated with hydrochloric acid. The ruthenium has then passed over as the volatile tetroxide. The residue is again heated with potash and nitre, and treated as before to remove the last trace of ruthenium.

The remaining blue powder (iridium oxide) is re-dissolved in aqua regia, evaporated to dryness, re-dissolved in water, and filtered. The dark solution is slowly poured into a concentrated solution of soda containing sodium hypochlorite (which should still remain *clear*), and distilled with a stream of chlorine, testing the distillate as before for ruthenium.

The greater part of the iridium is thus precipitated as the blue oxide, which is washed, dried, and subjected, in a porcelain or glass tube, to the combined action of carbon monoxide and dioxide evolved from a gently-heated mixture of sulphuric and oxalic acids. The iridium is thus reduced to metal, while the ferric oxide is unaffected. It is heated to redness with potassium bisulphate to remove iron and the last traces of rhodium; well washed, digested in chlorine water to remove any traces of gold, and in hydrofluoric acid to remove silica (accidentally introduced from the vessel or alkalis). It is then calcined at a strong red heat in a charcoal crucible, melted into an ingot, broken up, and boiled in hydrochloric acid to remove any iron which may have become attached during the breaking. The metal has then a sp.gr. 22·38, and contains a small quantity of platinum and minute traces of oxygen, ruthenium, rhodium, and perhaps of iron.

The isolation of the first considerable mass of iridium was effected by Mr. Edward Matthey, and the result was exhibited in the Paris Exhibition of 1855, in the form of an ingot. It formed a portion of the metal extracted from many thousands of ounces of platiniferous residues. Since then the refining and employment of iridium has become an industry practically inseparable from the working of platinum, the alloy of 10 p.c. iridium and 90 p.c. platinum having been selected after exhaustive trials for the standard weights and measures manufactured by Johnson, Matthey, & Co. for the Committee on International Standards.

These alloys were prepared by fusing, by means of the oxyhydrogen blow-pipe, a mixture of pure platinum and pure iridium in the required proportions, using slightly more iridium than required in the alloy to allow for loss from oxidation during the working. The alloy was subsequently carefully hammered and worked into the desired form, with all precautions to prevent the introduction of impurities and to ensure its homogeneity. To metallurgical chemists it will be interesting to note the extreme degree of purity attained in the large quantity of platinum (about 10,000 ounces) prepared for this purpose under the special supervision of Mr. George Matthey. M. Stas, of Brussels, analysed it on behalf of the International Committee, and stated that parts 1,000 parts of the mass contained 999·998773 of platinum—a result probably unsurpassed in metallurgical annals.

Matthey recommends for *standard rules* the alloy of iridium 15 p.c. and platinum 85 p.c., made in the tubular form; for *standard weights* the alloy containing 20 p.c. of iridium (*v. Alloys* of iridium). For an account of the means used for fusing such alloys, see Morin (C. R. 78, 1,502).

The following process was adopted by Deville and Debray for refining iridium (C. R. 81, 840). The finely-powdered metal is ignited with lead, and the alloy treated successively with nitric acid, aqua regia, and sulphuric acid. The residual crystalline iridium, free from osmium, is ignited with 4 parts barium oxide and 1 part barium nitrate, or with 5 parts of barium dioxide, in a silver crucible, mixed with 4 or 5 parts of water, subjected to a current of chlorine, and distilled when saturated. The ruthenium then volatilises as tetroxide, leaving green iridium trichloride. Sulphuric acid is then added, the liquid decanted from the precipitated barium sulphate, and evaporated to dryness. The brownish-red iridium *dichloride* remaining is taken up with water, treated with ammonium chloride, and the precipitate washed with concentrated ammonium chloride solution and calcined in a current of hydrogen. The metal is heated with potassium nitrate and potash in a silver crucible; the violet mass is taken up with water, and the residue washed successively with water, ammonium chloride, and oxalic acid, and finally with chlorine water and ammonia. It is then calcined in a carbon crucible and melted in the oxyhydrogen blow-pipe.

Properties.—Iridium is a white, steel-like metal of sp.gr. 22·39 (G. Matthey) or 22·42 (Deville and Debray), brittle when cold, somewhat malleable at a white heat. At a red heat it is superficially oxidised, but again becomes reduced at about 1000°C. It melts in the oxyhydrogen flame at 2500°C. according to Pictet. Iridium is used for the knife edges of delicate balances and other hard-wearing surfaces.

By exposure of a solution of iridium sulphate containing alcohol to light, the metal is deposited as an impalpable *iridium black*, more energetic in its action than platinum black. A minute portion of the washed and dried powder, when placed upon a paper soaked in alcohol will induce its combustion. Iridium unites with chlorine at a dull red heat; the pulverulent metal is oxidised on ignition with potash or potassium nitrate, with formation of potassium iridiate. Pure iridium is not soluble in aqua regia, but dissolves when alloyed with much platinum.

When held in the flame of a spirit lamp it produces a carbide of iridium, becoming dark-grey in colour, being penetrated with carbon and covered with black excrescences containing much iridium, which ignite on exposure to the air. The oxides are reduced to carbides when ignited in gases containing carbon.

Iridium forms three chlorides, each of which combines with alkaline chlorides. Four oxides are known whose solutions in acids and alkalis readily pass one into another, with change of colour.

Alloys.—Iridium alloys with most metals, increasing their hardness.

With *platinum* the alloys are of great importance. Iridium, even when present to the extent of less than 2 p.c., increases the hardness and indifference to reagents of platinum, and raises its melting point. The 10 p.c. alloy is used for making the most refractory platinum vessels; it has been used for the vents of Whitworth cannons and other heavy ordnance. Its durability is great; its elasticity equal to that of steel; its sp.gr. 21·615 (Deville and Debray); it takes a very fine polish. The 15 p.c. alloy was used in the preparation of the standard rules already mentioned. Its ductility, rigidity, and malleability are high; its sp.gr. 21·618 (Deville and Debray). The alloy of 20 p.c. iridium has an extremely high co-efficient of elasticity (22,200,000); its malleability and ductility are almost unlimited. On account of its high sp.gr. (21·614 Matthey), it is most useful for making standard weights. With 25 p.c. iridium, the alloy is hard to work. With 30–40 p.c. it is brittle when cold and hard to work, even near the melting-point. Its grain is extremely fine. A platiniridium alloy is used by Sellon for his gas-burner.

Iridium cannot be alloyed with *gold*. Great trouble is experienced by the Russian Government in the separation of the hard particles of osmiridium from the gold used for their coinage. Iridium can, however, be fixed to gold with ordinary silver solder.

With *copper* a hard brittle alloy is produced, suitable for hard-bearing surfaces, even when the proportion of iridium is small.

Osmium. Symbol Os. At. w. 190·3 (Seubert).

The mode of occurrence of this metal has been already described under iridium. Its separation from osmiridium depends on its property of forming a volatile tetroxide. Osmium is thus obtained as a by-product in the separation of the platinum metals. The distillate containing this oxide, obtained as already described (*Iridium*), is treated with ammonium sulphide and boiled. The precipitated sulphide is washed, dried, placed in a gas-coke crucible within a clay crucible, whose cover is well luted down, and the whole heated for four hours to the melting-point of nickel. The metal so produced may be rendered denser by heating in the oxyhydrogen flame. At the strongest heat of this flame osmium volatilises without previous fusion. As the tetroxide is intensely poisonous, all operations should be performed in a draught cupboard.

When heated with 5 or 6 parts of tin at bright redness it dissolves. On cooling and treating the mass with hydrochloric acid, the osmium is left as a hard crystalline powder.

The specific gravity is 22·43, *i.e.* higher than that of any other substance.

Osmium forms three chlorides and five oxides. The volatile tetroxide OsO_4 is formed when the metal is heated in the air or with potassium nitrate, or when solutions containing osmium are heated with oxidising agents. It forms colourless, acicular, transparent, flexible crystals, easily fusible, and freely soluble, boiling at 100°C. It forms weak combinations with alkalis, but is evolved from such solutions on boiling.

Ruthenium. Symbol Ru. At. w. 101·4 (Joly).

This metal is prepared by Deville and Debray (C. R. 83, 926) as follows:—Osmiridium, reduced to a fine powder by fusion with zinc (as described under *Iridium*), is heated for two hours, with a mixture of 3 parts barium oxide and 1 part barium nitrate to about the melting-point of silver. The cooled mass is finely powdered and added to dilute hydrochloric acid in a stoppered bottle and cooled to prevent the escape of osmium oxide. When all action has ceased, 1 part nitric and 2 parts sulphuric acid are added, the mixture shaken, settled, and decanted from the barium sulphate. About three-quarters of the liquid is then distilled off, the whole of the osmium being contained in the distillate. The equally-volatile ruthenium tetroxide is not produced under these circumstances.

To the residue is added 2 or 3 parts ammonium chloride and a little nitric acid, the liquid evaporated on a water-bath, and washed with a mixture of 1 part saturated ammonium chloride solution and 1 part water until the washings are colourless.

The residue, consisting of ammonium iridium and ammonium ruthenium chlorides, is ignited, and the residual metals are fused for two hours in a silver basin, with a mixture of 2 parts potassium nitrate and 1 part potash, and dissolved in water, leaving the bluish potassium iridiate. The solution is treated with nitric acid until the yellowish red colour due to potassium rutheniate is destroyed, and the ruthenium is precipitated as oxide containing silica and a trace of iridium and osmium. It is ignited in a graphite crucible, and fused by the oxyhydrogen flame.

Potassium rutheniate is obtained in the purification of iridium (*v.* Matthey's process) which may be reduced as above.

Ruthenium is a hard, brittle metal of sp.gr. 11·4 after fusion. It oxidises slowly in the air and burns with brilliant sparks, a smoky flame, and an odour of ozone when heated in oxygen. It may be obtained in crystals by fusion with tin, as described under *Osmium*. Ruthenium melts at about the same temperature as iridium. It is scarcely affected by aqua regia, but combines with chlorine at a red heat.

Ruthenium forms 3 chlorides and 5 oxides. The volatile tetroxide, frequently formed in the separation of this metal, is not produced, as is the case with osmium, by distillation of the solution with aqua regia. It distils over on passing chlorine through a heated alkaline solution of a ruthenium salt. It forms golden-yellow crystals, melting at 58°C. and boiling at about 100°C., but decomposing with explosion when the temperature reaches 108°C.

Rhodium. Symbol Rh. At. w. 102·7 (Jörgensen, Seubert, and Kobbé).

This metal is contained in the solution from the precipitation of platinum. The metals are co-precipitated by metallic iron, washed, mixed with 1 part lead and 2 parts litharge, and fused. Lead, copper, and palladium are removed from the mass by dilute nitric acid, and the residue is heated to redness for two hours, with 5 parts barium dioxide. It is cooled, lixiviated with water, and the residue is boiled and distilled with aqua regia to remove osmium.

The remaining solution is treated with sulphuric acid, decanted from the precipitated barium sulphate, evaporated at 100°C. with excess of ammonium chloride, washed with a solution of ammonium chloride until the washings are no longer red. The filtrate and washings are evaporated with sufficient nitric acid to decompose the ammonium chloride, and the residue is heated to redness with 3 or 4 parts of sulphur. Nearly pure rhodium remains on boiling the residue with aqua regia and sulphuric acid.

Properties.—Rhodium is a white, hard, malleable metal, fusing at about the same temperature as platinum and absorbing oxygen like that metal.

It is insoluble in aqua regia when pure, but soluble when alloyed with much platinum, or with oxidisable metals, such as bismuth or copper; according to Deville the alloy of platinum containing more than 30 p.c. of rhodium is insoluble in aqua regia.

Rhodium is readily attacked by chlorine. It combines with sulphur, but is again reduced to metal on strong ignition. When a solution of a rhodium salt is treated with sodium formate, the metal falls as a fine powder, which decomposes formic acid energetically into hydrogen and carbon dioxide, and, when heated, converts alcohol in presence of alkalis into hydrogen and alkaline acetate. According to Claus, only one definite chloride exists—the trichloride. Four oxides are known.

PLUMBAGO *v.* Graphite.

PODOPHYLLIC ACID, PODOPHYLLO-QUERCETIN, and **PODOPHYLLOTOXIN** *v. Podophyllum resin*, art. Resins.

PODOPHYLLUM RESIN *v.* Resins.

POLYCHREST SALT. An old name for normal potassium sulphate; applied also sometimes to Rochelle salt.

POLYGALIC ACID *v.* Senega.

POLYHALITE. A crystalline mixture in indefinite proportions of the sulphates of calcium, magnesium, and potassium occurring with rock salt in the Stassfurt salt deposits and other localities (*v.* Potassium, salts of).

POLYTELITE *v.* Freibergite.

PONCEAU *v.* Azo- colouring matters.

PONCEAU ANISIDINE *v.* Azo- colouring matters.

PONCEAU CRYSTAL *v.* Azo- colouring matters.

POPPY OIL. A fat drying oil obtained by expressing the seeds of the black poppy (*Papaver somniferum*), resembling olive oil in appearance and smell. Is used as an article of diet in South Germany and France, and is employed in painting after having been bleached by exposure to the sun in shallow vessels containing salt water.

PORCELAIN *v.* Pottery.

PORCELAIN CLAY *v.* Clay.

PORCELAIN STONE *v.* Clay.

PORPEZITE. A native alloy of gold and palladium.

PORPHYROXINE *v.* Vegeto-alkaloids.

PORPHYRY. A term loosely applied to any rock in which distinct crystals are embedded in a fine-grained ground-mass. The structure is well seen in many igneous rocks, where crystals have consolidated from a molten magma before the eruption of the mass. The typical porphyry of the ancients, *lapis purpureus*, contains crystals of white or pink felspar in a *purple*, crimson, or chocolate-coloured base, whence the original name *πορφυροῦς* or *πορφυρίτης λίθος*. It was extensively quarried by the Romans at Djebel Duchan ('Mountain of Smoke'), in Eastern Egypt, a locality described by Latin writers as *Mons porphyrites*; but though regarded as the most sumptuous of decorative stones, and largely used by Roman architects and sculptors for pillars, pavements, busts, and sarcophagi, it appears to have been unworked by the ancient Egyptians.

The crystals in the ancient red porphyry were analysed by Delesse, who found them to be a lime-soda plagioclase (Bul. Soc. Géol. France, 2 sér. 7, 484). The crypto-crystalline ground-mass contains much felspar altered to a reddish material, having the characters of epidote, and compared by Liebisch with the withamite, or red epidote from the porphyrite of Glencoe. Beautiful crystals of hornblende occur in the ancient red porphyry, and the rock may be described as a *hornblende-porphyrite*. Some varieties exhibit a brecciated structure, suggestive of an altered volcanic tuff, but referred by Rutley to the effect of crushing the rock and cementing the fragments *in situ* (Quart. Journ. Geol. Soc. 41, 1885, 157). The history of the rock has been fully worked out by O. Schneider (Ueber den roten Porphyr der Alten, Dresden, 1887). The Egyptian quarries have been visited and described by Williamson and other travellers (*v.* W. Brindley, Trans. R. Inst. Brit. Architects, 1888). Red porphyry, somewhat similar to the Egyptian, but less beautiful, occurs in the Sinaitic peninsula, at Elfdalen in Sweden, and in Siberia. The *porfido rosso antico* of Egypt is to be clearly distinguished from *rosso antico*, or the ancient red marble of Laconia.

The green porphyry of the ancients (*porfido verde antico*), known to Italian antiquaries as *serpentino*, was worked at Mount Taygetus in the Morea, and termed *lapis Lacedæmonius*. It contains white, or pale-green, crystals of plagioclase, embedded in a ground-mass filled with viridite, or chloritic products of the alteration of ferro-magnesian silicates. A similar, but less handsome, stone is the diabase-porphyrite of Lambay Island, near Dublin; the Lake District of Cumberland also yields a similar rock. Most of the rocks termed *porphyrites* are regarded by modern petrographers as altered forms of andesite, a type of volcanic rock allied to trachyte, but having its felspar plagioclastic and not orthoclastic.

The *quartz-porphyries*, belonging to the acid group of igneous rocks, and known in Cornwall as *elvans*, contain well-developed crystals of quartz, and often also of felspar, embedded in a felsitic ground-mass, consisting of a minutely crystalline aggregate of felspar and quartz. The elvans are sometimes worked as ornamental stones. Many granite rocks are beautifully porphyritic, and some of the Cornish granites owe their character to the presence of bold crystals of orthoclase. Fine crystals of pink and salmon-coloured orthoclase form the characteristic feature of the well-known porphyritic granite of Shap in Westmoreland, and of the handsome luxullianite of Cornwall. F. W. R.

PORPOISE OIL is obtained by heating the belly-blubber of the porpoise (*Delphinus Phocæna*) with water. Has a sp.gr. 0·937 at 16°, and when fresh possesses a pale-yellow colour and a smell of sardines. Becomes colourless on exposure to air, and acquires an acid reaction from formation of valerianic acid.

PORTLAND CEMENT *v.* CEMENTS.

PORTUGALLO OIL. Essential oil of orange-peel (*v.* OILS, ESSENTIAL).

POTASSIUM. Symbol K. At. w. 39·03 (Stas).

Occurrence.—Potassium occurs, principally as chloride and sulphate, in sea- and other natural waters, a litre of the former containing from 0·5 to 0·7 grms. of the element. As chloride or carbonate, or as an organic salt, it occurs in soils and vegetable and animal substances. Thus, wood ashes contain much potassium carbonate, which also forms a considerable proportion of the ash of marine plants, such as *laminaria* and *fuci*. Potassium occurs as *sylvine* or *sylvite* KCl, and as *carnallite* $KCl.MgCl_2 6H_2O$, especially in the beds overlying the great salt deposits of Stassfurt. As nitrate, it is found as an efflorescence on the soil, usually with the sodium salt, in Peru, Chili, &c., and as an important constituent of many mineral waters, such as those of Harrogate and Vichy. As the double sulphate of aluminium and potassium, it occurs in *alumstone* or *alunite* $3Al_2SO_6.K_2SO_4.6H_2O$, principally in trachyte and other rocks subjected to the action of sulphurous gases. It is found as bitartrate in wines, and as sulphate, carbonate, and chloride in beetroot molasses. As an organic salt (sudorate) it occurs in the 'suint' of sheep, and is separated therefrom as carbonate together with wool fat (*v.* Reports by the Juries on the Exhibition of 1862, p. 41, and Langbeck, S. C. I., 1890, 356).

The main source of potassium, however, is the primitive rocks, in which it occurs as *orthoclase* (potash felspar) $Al_2O_3K_2O.6SiO_2$; *muscovite* (potash mica) $K_2O.3Al_2O_3.4SiO_2$, *leucite* $K_2O.Al_2O_3.4SiO_2$; *apophyllite*

$$4(CaO.2SiO_2.H_2O)KF,$$

and other zeolites, and in many other silicates.

Manufacture.—The compound nature of the alkalis, and the presence in them of oxygen, had been suspected previous to 1807 (*v.* Lavoisier, Traité de Chimie, II. 194), but the isolation of potassium was not effected until that year, when Davy obtained it by electrolysis of the fused hydrate (T. 1808, 1; 1809, 39; and 1810, 16). The metal was soon prepared in larger quantity by Gay-Lussac and Thénard (A. Ch. 65, 325, and 66, 205) by slowly passing the hydrate over iron filings heated to whiteness in a gun-barrel protected by a luting of clay, their process being modified by Berzelius (Gilbert's Annalen, 6 (N. F.) 198), Mantell (Annals of Philosophy, Thomson and Phillips, 22, 232), Gmelin (Handb. 3, 5) and Tennant (A. 93, 291).

An important improvement was next introduced by Curaudau (A. Ch. 66, 97, and P. M. 1810, 36, 283), who replaced the iron by carbon or carbonaceous matter. This, and the other processes in use, were examined by Brunner (Bibliothèque Universelle de Genève (1823) 22, 36, and Schweigger's J. für Chem. und Phys. 35, 517), who also improved upon the apparatus employed by Bucholz (A. Ch. 73, 78), Trommsdorff (Gilbert's Annalen, 30, 333), Lampadius (Schweigger's J. für Chem. und Phys. 34, 221), and others.

Brunner's process, as improved by Wöhler (P. (1825) 4, 23, and 474), consists in carbonising potassium bitartrate in a covered vessel, and heating the resultant mixture of carbon and potassium carbonate with powdered charcoal in a mercury bottle, at the temperature of a powerful wind furnace. Kukla (Zeits. für phys. und verwandte Wissenschaften (1837), 5, 466), Werner (J. pr. 14, 267), Schœdler (A. 20, 2). Anthon (R. P. 58, 318) and Gale (Am. S. 19, 205, and 21, 60), proposed various arrangements and lutes for protecting the retort from the furnace, the two first, and Pleischl (Zeits. für phys. und verwandte Wissenschaften, 2, 307, and 343, 3, 326) also proposing modifications in the mixture used.

The method of condensing was next improved by Donny and Mareska (A. Ch. [3] 35, 147, *v.* also Mitscherlich, Lehrb. der Chem. 2, 10), who introduced the condenser described in the article SODIUM; while the addition of chalk to the mixture was found to facilitate the reduction by rendering the mass pasty instead of liquid, at the reduction temperature, thus preventing the separation of the carbon from the alkali (*v.* Deville, De l'Aluminium (Paris, 1859), 650, and Kühnemann, J. 1864, 180).

For the preparation of potassium of greater purity, Matthiessen (C. J. 1855, 8, 27) proposed the electrolysis of the easily fusible mixture of potassium and calcium chlorides.

The use of sodium instead of potassium for the manufacture of aluminium was introduced in 1854 by Deville (A. Ch. 1856, 46, 415), who also made many improvements in the manufacture of the metal. Since then, sodium has almost replaced potassium for use in the arts. The inconvenience and waste attending the manufacture of potassium, owing to the production of explosive compounds with carbon monoxide (*v.* Liebig, A. 11, 182, and Brodie, C. J. 12, 269), accounts to some extent for its high price. In Castner's process, the proportions used are such that no carbon monoxide is formed during the reaction, so that potassium can now be produced at a price not greatly exceeding that of sodium.

The various processes employed in the preparation of potassium are identical with those used in sodium manufacture, and are described, together with a list of patents and other matters relating equally to both metals, in the article Sodium.

The crude potassium obtained by any process in which carbon monoxide is a constituent of the evolved gases, always contains the explosive compound above mentioned, which renders it liable to detonate on the slightest friction. For this reason, it must be redistilled, once or twice, when so prepared.

Properties.—Potassium, when freshly cut, has a brilliant, silvery metallic lustre. It crystallises in obtuse octahedra, showing a greenish-blue tint (Long, C. J. 1860, 13, 124).

According to Baumhauer (B. 6, 655), its sp.gr. at 13° is 0·875. At 0°, potassium is brittle, and possesses a crystalline fracture. At 15°, it acquires a waxy consistency, and a few degrees higher becomes pasty, melting at 62·5° (Bunsen, J. 16, 178) and boiling at 719–731° according to Carnelley and Carleton Williams (C. J. 1879, 565), or at 667° according to Perman (C. J. 1889, 328). The vapour has a green colour, and attacks glass and porcelain. Its characteristic channelled absorption spectrum has been examined by Roscoe and Schuster (Pr. 22, 362, and C. N. 29, 268).

Its molecular weight as determined by Raoult's method, using mercury as a solvent, is between 29·1 and 30·2 (Ramsay, C. J. 1889, 533). The lowering of the melting-point of potassium by the presence of sodium, gold, and thallium has been determined by Heycock and Neville (C. J. 1889, 666).

Potassium dissolves in liquefied anhydrous ammonia forming a deep-blue solution, from which the metal is re-obtained on evaporation of the ammonia (Seeley, C. N. 23, 169). It is the most electro-positive element known with the exceptions of cæsium and rubidium, and is an extremely powerful reducing agent. Hence the use of potassium for the preparation of less electro-positive elements, such as boron, silicon, magnesium, aluminium, &c., for the reduction of gases containing oxygen and of organic and other compounds.

On exposure to the air, it rapidly becomes converted into the hydrate and finally into the carbonate. It decomposes water with sufficient energy to ignite the liberated hydrogen. When carbon dioxide is passed over heated potassium, it is reduced to carbon, with formation of potassium oxide.

Potassium unites directly with the halogens and with sulphur, selenium, tellurium, and phosphorus, burning brilliantly when heated with them. When heated in carbon monoxide, it forms a black mass identical with the explosive body produced in the manufacture of potassium.

Alloys.—Potassium alloys with most metals, usually by being heated with them. The more important alloys are described under the various metals. With *sodium*, potassium forms alloys of low melting-point, as observed by Davy. Greville Williams (C. N. 3, 21) has obtained an alloy melting below the ordinary temperature and containing about one fourth its weight of potassium, by heating sodium with potash to about 171°; while Wanklyn (C. N. 3, 66) has obtained a similar alloy by heating sodium with potassium acetate.

Potassium combines directly with *mercury*, with evolution of heat. The melting-points of a number of these amalgams have been determined by Merz and Weith (B. 14, 1445). When containing 70–96 parts of mercury to 1 part of potassium, the amalgam is crystalline. With 30 parts of mercury, it is hard and brittle. When heated to 440°, they all leave a crystalline amalgam of the composition HgK_2, spontaneously inflammable on exposure to the air (De Souza, B. 9, 1050), but all the mercury is evolved below a red heat. Kraut and Popp (A. 159, 188) have prepared a crystalline amalgam of the composition $Hg_{24}K_2$.

POTASSIUM, SALTS OF. The sources from which potassium salts are obtained for technical purposes are—firstly, the sea-water; secondly, the mineral crust of the earth; thirdly, the vegetable, and to some extent the animal, kingdom.

The quantity of potassium salts contained in *sea-water* is not very large, but it has been found economically possible to extract it therefrom, as we shall see in *potassium chloride*. Indirectly, the potassium salts obtained in the working up of kelp are derived from this source.

The mineral crust of the earth contains potassium in the state of *silicates*, as a constituent of several of the most important minerals, as felspar and mica. By the decay of the rocks containing those minerals, potassium compounds have been spread all over the earth as part of the arable soil; from this source are derived, not only the potassium compounds contained in all plants, but probably most of those contained in sea-water. The importance of this occurrence of potash is enormous for the existence of all organisms; but it has not been possible so far to extract potassium compounds for technical purposes from the natural silicates or the arable soil.

Several other salts of potassium are, however, more adapted for this purpose. Potassium *nitrate*, as found in the crude state, especially in India, is certainly more valuable in respect of its acid than of its alkaline constituent; but the latter is also very important, as is best proved by the large quantity of potassium chloride employed for the manufacture of artificial saltpetre.

Potassium sulphate occurs in large quantities in alum rock, and in several of the minerals found together with carnallite in the Stassfurt deposits.

Potassium chloride is found both in the pure state, as *sylvin*, and in much larger quantities as *carnallite*, in the Stassfurt deposits and some other places. This is at present the most important of all the sources from which potassium salts are obtained for technical purposes.

In the *vegetable kingdom* potassium is universally found, principally in the liquid contents of the cells and vessels, chiefly combined with organic acids. On burning it appears in the ashes as carbonate, together with more or less sulphate, chloride, phosphate, and silicate. It is unnecessary to say that all this potassium is derived from the soil on which the plants grow; but for many centuries, indeed, apart from saltpetre and kelp, nearly up to the middle of this century, wood ashes formed practically the only source of potassium compounds employed for technical purposes. Even at the period stated it was, in the first instance, another vegetable source which was opened out for potassium compounds—viz., the *vinasse*—that is, the residue left on distilling fermented beet-root molasses. Hence the expression 'vegetable alkali,' by which potash was distinguished from soda when Duhamel, in 1736, had proved the separate existence of those bodies, was altogether appropriate, not only at this time, but even much later, until the Stassfurt discoveries made that designation altogether unsuitable.

Even the animal kingdom contributes a certain quantity of potassium compounds, in the shape of the carbonate of potash from the 'yolk' of *sheeps' wool* (*suint*).

Potassium chloride. This salt, which in commerce is generally known as '*muriate of potash*,' was formerly obtained as a by-product in various manufactures, as in the working up of kelp for iodine, from the spent ley of soapmakers, in refining native saltpetre, &c. The quantities thus obtained were not very large, if compared with the present state, and they were principally used in the manufacture of alum and of potassium chlorate. Some more potassium chloride was afterwards obtained in Balard's process of working-up the mother-liquors from the manufacture of sea-salt, and a good deal more in the manufacture of potashes from vinasse (*cf. Potassium carbonate, infra*).

But all this sinks into insignificance beside the enormous quantities obtained from the *Stassfurt carnallite*, and we shall therefore here describe the Stassfurt occurrence of potassium salts, as well as the methods of manufacture pursued there.[1]

The village of Stassfurt is situated on the river Bode, not far from Magdeburg, in Prussian Saxony, close to the borders of the small principality of Anhalt. In 1850 Stassfurt numbered 2,000 inhabitants, in 1885, 16,000, and the adjoining newly-formed village of Leopoldshall (in Anhalt), 4,000 inhabitants. The Stassfurt brine-springs are mentioned as far back as 1227, and in the last century 7,000 tons of salt per annum were made there in 30 salt-pans; but about 1815 the production of salt from brine was stopped there, having ceased to be remunerative in the face of competing brine-springs. In 1839 the Prussian mining office commenced boring for rock-salt, and in 1843 the salt was struck at a depth of 850 feet. The boring was continued for another 1,080 feet without getting to the bottom of the stratum of salt; but the brine pumped up was extremely impure, containing, together with sodium chloride, a large quantity of magnesium chloride, potassium chloride, and magnesium sulphate. It was, however, conjectured at once that these salts might be deposited in separate strata, and it was resolved to sink two shafts. These were commenced in 1852, and within five years they had reached a thick stratum of pure rock-salt, after having penetrated a number of strata of other salts, of an aggregate thickness of 530 feet, which were called 'abraumsalze,' because they were at first considered useless, and had to be taken away before getting to the rock salt.

Later on it was found that the salt deposits occupy an enormous basin in the North German Plain, which has been successfully tapped in several other places, of which we mention only Sperenberg, near Berlin, where the boring was continued through the enormous thickness of 3,940 feet of salt without getting to the bottom; also at Segeberg, near Lübeck, and in other places. But the potassium-bearing 'abraumsalze' have appeared only in the vicinity of Stassfurt, in the Upper New Red Sandstone, where the following shafts have been opened:—

In 1856 and 1857, the two Prussian shafts at Stassfurt; in 1861, the Anhalt shaft at Leopoldshall; in 1876, two shafts at Douglashall, near Westeregeln; in 1876, a shaft at Neu-Stassfurt; in 1878–1883, another two shafts at Stassfurt; in 1883, a shaft at Aschersleben, sunk by the Continental Diamond Rock-Boring Company; some more shafts at Solvay's mines, near Bernburg, at Schönebeck, &c.; the Hercynia shaft at Vienenburg.

The profiles (figs. 1 and 2) give an idea of the strata pierced in the two oldest and most important shafts at Stassfurt and Leopoldshall.

At Stassfurt itself the total thickness of the salt strata is estimated at about 2,500 feet, and the time necessary for their formation at about 8,000 years. F. Bischof, who has examined them most thoroughly, divides them into the four following 'regions,' of which only the first and the last have become of technical importance.

1. *Anhydrite or rock-salt region*, so called from the strings of anhydrous calcium sulphate which divide the rock-salt into bands of an average thickness of nearly 4 inches, each of which is supposed to be a year's growth. The layers of calcium sulphate are only one quarter inch thick, and amount only to 4 per cent. by weight of the rock-salt in the upper strata, or 9 per cent. in the lower strata. By mechanically separating the anhydrite, rock-salt of 99 per cent. NaCl can be obtained on a large scale. Small quantities of hydroboracite ($CaMgB_6O_{11}, 6H_2O$) and of strontium sulphate are found here as well. The thickness of this stratum varies a great deal; in the centre of the basin it may be estimated at about 2,000 feet.

2. *Polyhalite region*. Here the rock-salt is already mixed with mother-liquor salts, of which the dominant one is *polyhalite*,

$$2CaSO_4, MgSO_4, K_2SO_4, 2H_2O.$$

Magnesium chloride accompanies the rock-salt, and small quantities of brimstone and of bituminous substances are found here. The average composition of this stratum is: 91 rock-salt, $6\frac{2}{3}$ polyhalite, $\frac{2}{3}$ anhydrite, $1\frac{1}{2}$ magnesium chloride; its thickness is 207 feet.

3. *Kieserite region*, so called from the occurrence of white bands of kieserite, $MgSO_4, H_2O$. The average mixture is:

65	per cent.	rock-salt
17	,,	kieserite
13	,,	carnallite
3	,,	bischofite, $MgCl_2, 6H_2O$
2	,,	anhydrite.

This stratum has a thickness of 187 feet.

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[1] In this part we follow to a great extent the detailed description by Pfeiffer, in his 'Handbuch der Kali-Industrie,' Braunschweig, 1887 (*cf.* also, for some details, Hake, S. C. I. 1883, 146; and Borsche, S. C. I. 1888, 296).

4. *Carnallite region.* This contains 55 p.c. of *carnallite*, $KCl,MgCl_2,6H_2O$, the most valuable of the Stassfurt salts, together with 25 p.c. rock-salt, 16 p.c. kieserite, the remaining 4 p.c. consisting of magnesium chloride (*bischofite*), magnesium bromide, *tachydrite*

$$(CaCl_2,2MgCl_2,12H_2O),$$

boracite or *stassfurtite* ($2Mg_3B_8O_{15}+MgCl_2$), anhydrite, *reichhardtite* ($MgSO_4,7H_2O$), clay, sand, micaceous oxide of iron, &c. The thickness of this stratum is 140 feet.

In some places the action of water has produced important changes in this region which have replaced the kieserite and part of the carnallite by *kainite*, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$ (about 55 p.c. of the whole), part of which has passed over into *schoenite*, $K_2SO_4,MgSO_4,6H_2O$. In other places the magnesium chloride has been washed out entirely, and the mixture contains 20 per cent. of pure potassium chloride, *sylvin*, with 30 to 40 p.c. of rock-salt, and an equal quantity of kieserite and other impurities. Only exceptionally *astrakanite*

$$Na_2SO_4,MgSO_4,4H_2O,$$

is found.

The salts are covered by from 20 to 33 feet of *salt-clay*, over this from 133 to 300 feet of *anhydrite*, and this again by 80 to 100 feet of very pure, transparent *rock-salt*, free from calcium sulphate, evidently a secondary formation.

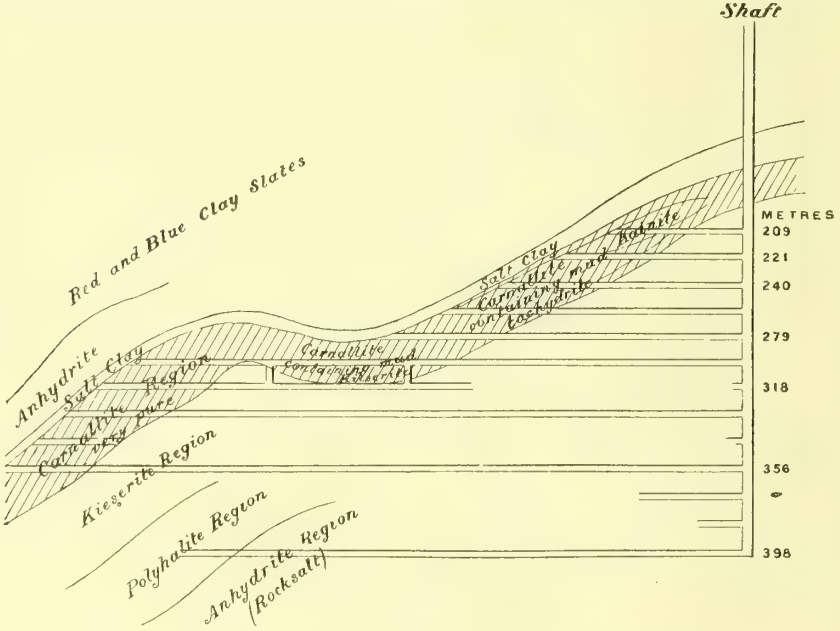


FIG. 1.

Formation of the Stassfurt deposits.—There can be no doubt that the formation of the salt deposits of the North German Plain has been caused by the evaporation of sea-water. But there must have been special causes why, in a comparatively small part of that large area—viz., in the vicinity of Stassfurt — potassium and magnesium salts have been separated in large quantities, whilst on the greatest part of the ground only rock-salt and anhydrite are found.

According to Regnault, the average composition of sea-water is:

Total percentage of solids	3·53
consisting of:	
Sodium chloride	76·49
Potassium chloride	1·98
Magnesium chloride	10·20
Magnesium bromide	0·06
Magnesium sulphate	6·51
Calcium sulphate	3·97
Calcium bicarbonate	0·08
	99·29

We find here all the materials for the formation of the Stassfurt deposits, whose average composition has been stated by Bischof, as follows:

	Percentage expressed in minerals
Rock-salt	85·1
Anhydrite	3·7
Polyhalite	0·8
Kieserite	3·3
Carnallite	6·2
Magnesium chloride	0·9

	Percentage expressed in salts
Sodium chloride	85·1
Potassium chloride	1·7
Potassium sulphate	0·2
Magnesium chloride	2·6
Magnesium sulphate	3·1
Calcium sulphate	4·0
Chemically-combined water	3·3

Since Bischof's time the bottom of the deposit has been reached, and it can now be said that the percentage of sodium chloride and of calcium sulphate is much higher than he assumed.

If we compare the composition of the Stassfurt deposits with the results of the artificial evaporation of sea-water as carried out in 1849 by Usiglio (A. Ch. [3] 27, 92), we find that there are some differences, partly caused by the long duration of the natural process and its yearly interruption, partly by the loss of mother-liquor (see below). The various salts were transformed into the minerals now present by a subsequent loss of water and by their mutual interaction, and a regular succession of those minerals was formed through long periods, caused by the autumnal influx of fresh sea-water. One remarkable difference is also this: while in artificial evaporation the calcium sulphate is entirely precipitated at an early stage, it is formed at Stassfurt even in the strata consisting of mother-liquor salts. Why the calcium sulphate at Stassfurt is in the form of anhydrite, not in that of gypsum ($CaSO_4,2H_2O$), as in the artificial evaporation of sea-water, we understand now from the observations of Hoppe-Seyler (Chem. Centralbl. 1866, p. 217) and Rose (*ibid.* 1871, p. 613), according to which the hydration water of gypsum is abstracted from it by contact with a *nearly-saturated* solution of sodium chloride, a condition which we must assume to have existed at Stassfurt.

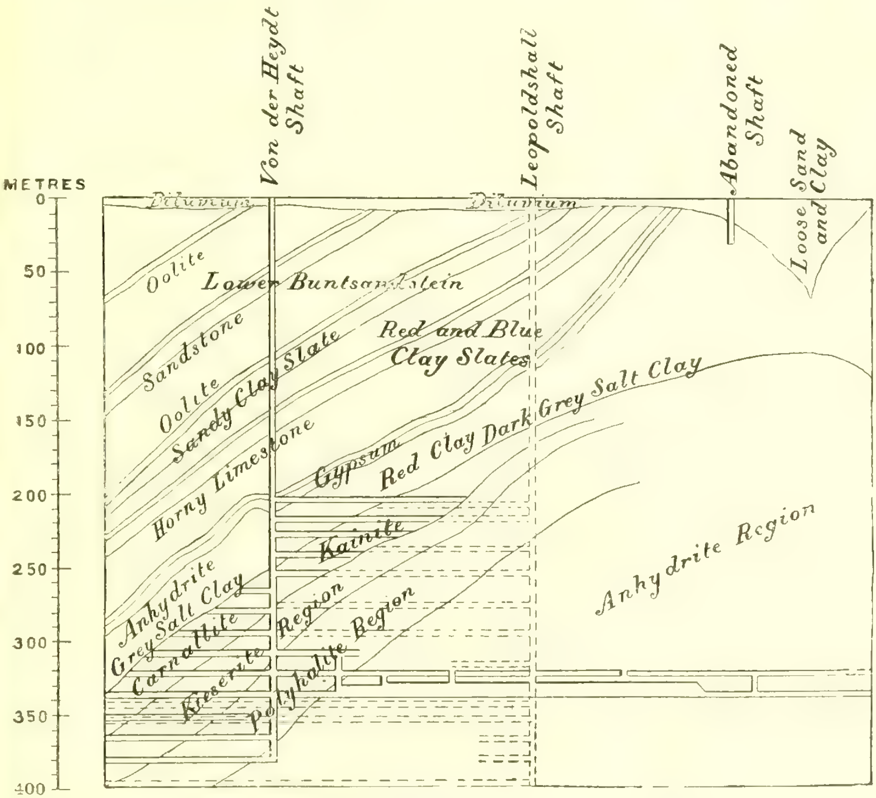


FIG. 2.

It is quite evident that the Stassfurt deposits have not been formed by the simple evaporation of a basin of normal sea-water, which would have been required to possess a depth of about 30 miles, and which would have produced a very different arrangement of salts. There must have been conditions similar to those even now found present in some of the Sarmatian lakes. Thus Göbel found at the bottom of Lake Elton a salt deposit of a thickness of 12 feet, consisting of 100 annual layers, which increased in strength and hardness from the top downwards, and at the bottom were as hard as stone. This lake is filled with a saturated brine; by the surface-evaporation in summer, crusts of common salt are formed, which sink to the bottom. Later on, the common salt gets mixed with Epsom salt and other mother-liquor salts, which form a porous, bitter, and deliquescent layer. The autumnal rains and floods partly dissolve and partly densify this top layer, and at the same time cover it with black mud, thus forming a distinct boundary line upon which the next year's crusts are formed again. In spring the water of that lake contains 13·5 p.c. sodium chloride and 10·5 p.c. of magnesium chloride; in autumn it holds but a small quantity of liquor, containing only 4 p.c. NaCl, with 20 p.c. $MgCl_2$.

The nearest approach to the Stassfurt conditions is found in the Adji-Darja Bay, in the east of the Caspian Sea, a bay of a superficial area of 2,000 or 3,000 sea miles, and almost entirely separated from the Caspian by a bar. There is, however, a small channel through which the water, abstracted by the intense evaporation within the bay, is replenished from the Caspian. This causes a continuous separation of salt, which is estimated by Schleiden at about 400,000 tons per diem, and the formation of a mother-liquor, part of which finds its way back into the Caspian. Where the depth of the bay is greater the concentrated liquor sinks to the bottom, causing a state of sursaturation at this place and the deposition of mother-liquor salts. Without this, practically all the mother-liquor would flow back over the bar, and no mother-liquor salts would be formed; and this seems to have been the condition of most of the rock-salt, forming basins of former geological periods. In the case of the Stassfurt salts we must undoubtedly assume an *intermittent* influx of water, and also a number of geological elevations and depressions of level in order to account for the succession of the various strata. We may, with very great probability, assume the following play of causes: the Stassfurt basin was a valley, inclosed by two longitudinal folds of the earth's crust, communicating at one end with the ocean by a shallow bar, over which, in autumn, the gales and high tides carried large quantities of sea-water; not sufficient, however, to replace the water lost by evaporation. For a long period only gypsum was deposited here; afterwards common salt was formed as well, which converted the gypsum into anhydrite, but which for a long time was re-dissolved every autumn by the dilution of the liquor, caused by rain and floods. Thus the thick crust of gypsum and anhydrite was formed which lines the bottom of the basin. Later on, the liquor became more and more concentrated; the crusts of common salt now became permanent, and the yearly deposits increased in thickness. The sursaturation of the liquor at the bottom caused the transformation of the common salt into rock salt (as first proved by Mohr). Just as we observe it now in the 'salt gardens' on the Mediterranean, the last portions of the summer salt contained a little gypsum, but the greatest quantity of gypsum was precipitated when the strong brine came into contact with fresh sea-water breaking over the bar, thus forming a distinct line of separation against the next year's deposits in the shape of the 'anhydrite strings.' Since there was less and less room in the basin for fresh sea-water, those strings decreased in thickness during this period, which must have lasted several thousands of years, during the later part of which the yearly deposits had an average deposit of 3½ inches. Owing to further concentration of the liquor the crusts of salt in the later part of summer were more and more mixed with Epsom salt, which appears also with the gypsum precipitated soon after by the influx of fresh sea-water. In this period, which must have lasted 500 or 600 years, *polyhalite*

$$K_2SO_4,MgSO_4,2CaSO_4,2H_2O$$

was formed in the following way: some carnallite, $KCl,MgCl_2,6H_2O$, formed in summer, was at that period always decomposed in autumn by fresh sea-water, and the potassium chloride thus set free and coming into contact with the just-deposited Epsom salt was converted into potassium sulphate, which met with enough magnesium and calcium sulphate to form polyhalite. Exceptionally, indeed, carnallite is actually found in that region. During the next period of 500 years, with increasing concentration, some carnallite is regularly found, but the principal deposit at that time consisted of *kieserite*

$$MgSO_4,H_2O.$$

It has been proved by Precht (Ber. 14, 2,131) that from a concentrated solution of magnesium chloride such as must have filled the basin at that period the magnesium sulphate is separated by evaporation, not in the state of Epsom salts ($MgSO_4,7H_2O$), but in that of kieserite. This compound being insoluble, as well as the anhydrite, the formation of polyhalite was not any more possible.

During the fourth and last period of 500 years, when there was less room for the influx of fresh sea-water, the formation of *carnallite* got the upper hand. Pfeiffer has proved that that salt, and even magnesium chlorhydrate, can be made to crystallise by spontaneous evaporation at the temperature of hot summer days in our present climate. The formation of carnallite must have been still abundant, and a deep layer of mother-liquor, in which magnesium chloride prevailed, must have been standing over the potash-bearing strata when new geological changes caused the eruption of a mighty mass of clayey mud, charged with organic substances, which sank to the ground, forming a layer of salt clay, 26 feet thick, which protected the underlying strata against a subsequent solution of the salts previously deposited, even after the mother-liquor had run off. The loss of that liquor accounts for the difference between the average composition of the Stassfurt deposits and that of the sea-water (comp. above). Wherever such accidental protection was not afforded, the surface-water must have re-dissolved the upper strata, which accounts for the general absence of mother-liquor salts in other localities.

Apart from Stassfurt, the following occurrences of potassium salts require mentioning:—

In 1866 at *Kalusz*, in Eastern Galicia, potassium salts were found in large quantities, principally consisting of sylvin and kainite, and a large manufacturing industry was commenced on the strength of this. But the quality of the salt proved inferior to the first samples, and in 1875 the works were discontinued, for various reasons, as being unable to compete with Stassfurt.

Small quantities of potassium salts, always of poor quality, have been found in the Punjab, in Persia, and in Colorado. None of these give any promise of industrial application.

The mines round Stassfurt in their present extension are equal to a daily output of 9,000 or 10,000 tons. In 1883 there were about 4,000 men employed in the mines, and about 2,000 men in the potash works. The *rock-salt* is not now obtained from the lower strata, where the admixture of anhydrite brings it down to 95 p.c., but from the upper (secondary) strata at Neu-Stassfurt, where it comes up to 99 p.c. of real sodium chloride. There is also a large quantity of pan-salt made in the neighbouring Schönebeck salt works. The following figures give the official returns of the minerals got in that district for some years (in metrical tons of 1,000 kilog.):—

Year	Rock-salt	Carnallite, Kainite, and other mother-salts	Kainite alone
	Tons		
1875	77,705	529.212	23,818
1876	76,656	583,662	17,776
1877	80,525	807,504	33,305
1878	101,694	770,329	32,480
1879	107,471	661,466	48,828
1880	118,170	668,540	137,795
1881	149,227	905,223	155,301
1882	141,328	1,212,556	144,757
1883	157,666	1,191,009	226,600
1884	344,798	979,597	203,040
1885	377,491	920,944	242,281
1886	444,397	945,271	240,421
1887	405,420	1,080,104	239,412
1888	414,557	1,235,336	318,576
1889	544,591	1,185,750	324,477

The following minerals form the staple production at Stassfurt:—

The average composition of *crude carnallite* is:

	Per cent.
Potassium chloride	15·7
Sodium chloride	21·5
Magnesium chloride (with a little bromide)	21·3
Calcium chloride	0·3
Magnesium sulphate	13·0
Insoluble	2·0
Water	26·2

It is sold on a basis of 16 p.c. potassium chloride, and its price ranges about 10*s.* per ton.

Crude kainite generally contains:

	Per cent.
Potassium sulphate	24·0
Magnesium sulphate	16·5
Magnesium chloride	13·0
Sodium chloride	31·0
Gypsum and clay	1·5
Water	14·0

Its price for exportation is rather below 20*s.* per ton, and somewhat less for home consumption.

Crude kieserite is very impure, much more so than the residual product obtained in the manufacture of potassium chloride. Still, about 12,000 tons per annum are sold at 8*s.* or 9*s.* per ton.

Boracite, with 52 or 53 p.c. crystallised boracic acid, is obtained as a by-product. In 1883 205 tons were got, and were sold at about 30*l.* per ton.

The importance of the Stassfurt potash industry is best illustrated by the following statement. Joulin (Bl. 1866, pp. 100, 359) calculates the yearly manufacture of potassium chloride before the rise of Stassfurt as follows:

	Tons
From vinasse	1,200
„ sea-water	400
„ varech (France)	1,500
„ kelp (Scotland)	1,200
	4,300

[The chloride manufactured from kelp is estimated much too low.]

But the average production of the Stassfurt manufacture of potassium chloride between 1878 and 1883 has amounted to 120,000 tons per annum. We shall give more statistical details at the close of this chapter.

The manufacture of Potassium chloride at Stassfurt.

At first the importance of the strata found underlying the rock-salt at Stassfurt was not recognised, and it is principally due to the untiring exertions of Dr. A. Franck since 1860 that this was ultimately done. In 1861 he erected a small factory, and was immediately followed by Messrs. Vorster & Grüneberg, and soon after by Messrs. Leisler & Townsend. The last-mentioned factory—called the 'English factory'—which was designed on the principle of introducing as much as possible mechanical in lieu of manual labour was very important for the later development of that industry. In 1864 there were already 18, in 1872 33 different potash works at Stassfurt, in 1887 the number was 35. The price of the crude salt commenced with 16*s.* per ton; it went down to 8*s.*, and in 1879 went up again to 10*s.*, about which figure it stands still. The quantity of potassium chloride produced has undergone many oscillations; it has been highest in 1882, when 153,356 metrical tons were made. The selling price for 80 p.c. potassium chloride was 18*l.* per ton in 1861, 5*l.* 10*s.* in 1877, 6*l.* 17*s.* in 1884, 6*l.* 16*s.* in 1888. In 1887 the daily consumption of carnallite was 2,750 tons.

The raw material for that manufacture is the crude carnallite as supplied by the mines in tolerably uniform quality; its average composition has been stated above. The principles of working it up are as follows: carnallite, $KCl,MgCl_2,6H_2O$, is unstable in the presence of water; it is decomposed into a magma of very finely crystallised potassium chloride and a solution of magnesium chloride, retaining but little KCl at a low temperature. On heating the solution dissolves much more KCl, and on cooling the latter salt is separated in much larger crystals, so long as the proportion of $MgCl_2$ does not exceed three times that of KCl. When that proportion has been reached the liquor on further concentration yields a crop of carnallite, which at a low temperature is very little soluble in the remaining solution of magnesium chloride. Of the foreign salts present in crude carnallite, rock-salt is much less soluble in hot $MgCl_2$ solution than KCl, and thus remains behind to a great extent; kieserite, which is insoluble as such, but turns into soluble Epsom salt by heating it with pure water, is prevented from this by the presence of magnesium chloride. The remaining substances are not of much consequence; some of them are quite insoluble.

Practically it has been found useful to treat the ground raw material, not with water, but with waste liquor from a previous operation in such quantity that it suffices for dissolving the carnallite present at a boiling heat; the solution is separated from the residue (the washings being utilised for a fresh solution) and is allowed to cool down, when it deposits about 80 p.c. of the potassium chloride; the mother-liquor, on further evaporation and cooling, yields the whole of the remaining KCl as a crop of carnallite, which is decomposed by water as above. The products are purified in the manner described below.

The first operation, *dissolving the crude carnallite*, is the most important of all for the success of the manufacture. The result differs very much according to the quality of the crude carnallite, according to its state of division, according whether pure water or liquors obtained in other stages of the manufacture are employed, and also according to the duration of the operation. It is, in principle, preferable to effect the solution of the carnallite as quickly as possible in order to dissolve less of the other salts. The quickest operation is undoubtedly that practised at the 'English' factory—crushing the crude carnallite into powder, and dissolving it in a close vessel at several atmospheres' pressure with mechanical agitation. But this process causes too much rock-salt and even kieserite to be dissolved at the same time, and it also causes the formation of very much mud; hence most manufacturers work at the ordinary atmospheric pressure, or very little above it, without mechanical agitation, and employ coarsely-broken carnallite.

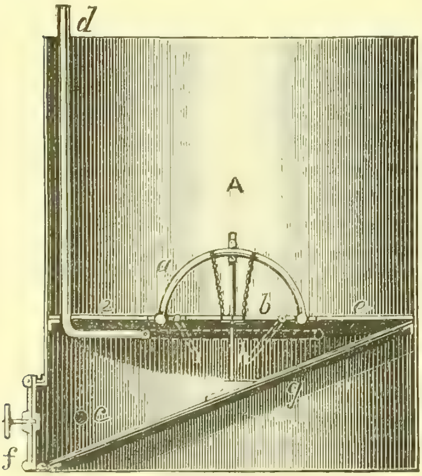


Fig. 3.

Fig. 3 shows one of the best descriptions of dissolver, on a scale of $\frac{1}{50}$. The true bottom *g* is slanting, the false bottom *e* is horizontal. The latter is perforated by a large number of holes $\frac{1}{3}$-inch wide; in the centre there is a double-hinged trap-door *b*, also perforated. The two halves of this door are suspended from the hinged arm *a*; they are closed when *a* is in the upright position, in which it is kept by the vertical rod *h*. When the liquor has been run off through *c*, the man-hole *f* is opened and the rod *h* is knocked away, which causes the arm *a* to turn over, and the two halves of *b* fall down. The residue is now easily washed down from *e*, and cleared out through *f* by a strong jet of water passed all over *e* by means of a hose. The steam-pipe *d*, with two rows of holes, is carried round the central opening of *e*. The conical shape of the bottom has the two-fold advantage that the liquor can be run off completely and that the residue can be got out very quickly.

Where it is considered desirable to dissolve under a slight pressure, the top of the dissolver is covered in, the man-hole being closed during the work, or else a tube reaches down from the cover into the liquid, nearly to the false bottom, in order to introduce the salt, and to produce some degree of steam pressure in the apparatus. The waste steam can be employed for heating up the dissolving-liquor in another pan. Such vessels, of a capacity of about 350 cubic feet, admit of working up 50 tons of salt and more per 24 hours.

The liquor employed for dissolving (called 'Löselauge') is a mixture of various liquors resulting in the manufacture, especially the washings of the first residue, and those of the potassium chloride, as well as various mother-liquors, altogether of a specific gravity 1·268 to 1·279; through being heated up by waste steam, the liquor comes down to 1·257, and is used in this state. This liquor is run into the dissolver till this is half full; steam is injected till the liquor is brought to boil, and only then the crude carnallite is introduced. For each 100 cubic feet of tank room, from 30 to 36, or at most 42 cwt. of carnallite can be charged. The solution is first brought to specific gravity 1·313 to 1·337 (measured hot and in the muddy state), but in this state the residue would be very difficult to treat; there would be considerable loss of potassium chloride by crystallising out before the liquor was clarified, and the potassium chloride obtained in the coolers would be contaminated by newly-formed carnallite. To avoid this, the solution is diluted to specific gravity 1·28 or 1·30 (measured hot and muddy). The operation of dissolving ought not to last more than half an hour.

The solution must now be clarified by allowing it to rest for an hour or two in settling-vessels, and drawing off the clear portion by means of a drop-siphon. The clarifying operation can be promoted by sprinkling a little milk of lime on the surface, which precipitates some magnesia, the latter carrying down the other impurities. The residue must be once or twice boiled up with fresh water, if the crude carnallite had been employed in lumps of the size of a fist; if, as now usual, it had been more finely crushed, it is either removed at once, or it is previously boiled up with a small quantity of mother-liquor, the resulting liquor being utilised as part of the dissolving liquor for fresh carnallite, or by cooling down, when it yields weak potassium chloride.

The following analyses show the composition of the ultimate residue, forming from 26 to 30 parts of the crude carnallite:

	a	*b*	*c*
Potassium chloride	5·25	3·0	2·2
Sodium chloride	47·00	45·0	54·8
Magnesium chloride	3·85	2·0	2·5
Magnesium sulphate	29·25	38·0	22·9
Calcium sulphate	2·15	0·7	1·8
Insoluble	6·00	5·3	5·0
Combined water	6·50	6·0	10·8
	100·00	100·0	100·0

a is a product as formerly obtained, *b* and *c* more recent products of different works. The 'insoluble' is mostly anhydrous calcium sulphate, clay, boracite, and sand.

The residue was formerly allowed to accumulate in large heaps, some part of which only was utilised for manufacturing kieserite and sodium sulphates; where there was not room enough for depositing it, it had to be washed away by a stream of water. Recently, it is largely employed for filling up the old workings in the carnallite mines, since this has been required by Government regulations in order to prevent subsidences of the soil.

A different kind of residue is obtained by thoroughly settling the liquid in tanks, protected against cooling, and drawing off the clear liquor by means of a drop-siphon. This second residue, the 'kieserite mud,' consists essentially of kieserite, accompanied by a little anhydride, clay, boracite, gypsum, sodium chloride, &c.; also by potassium chloride. It is separated from the liquor by means of a vacuum filter, or, preferably, of a filter-press in which it can also be washed by hot mother-liquor, which removes the potassium chloride without affecting the other salts to a great extent. Even then from 4 to 16 p.c. of potassium, calculated as chloride, are retained in the mud, probably in the shape of potassio-magnesium sulphate.

Formerly the clear liquor was purposely allowed to cool down to some extent before being run into the crystallising-vessels, say to a temperature of 80°C. or even less, in order to precipitate some sodium chloride. But since the solution is now made by means of mother-liquors, the clear liquor contains less NaCl, and is generally at once employed for crystallisation. The following analyses refer, I. to a liquor made with water, of specific gravity 1·3 (at 105°C.) in the muddy, and 1·284 in the clarified, state; II. to a liquor made with mother-liquor, of specific gravity 1·313 (at 105°C.) before being diluted with water; III. shows the maximum and minimum percentages found in ordinary liquors:

	I.	II.	III.
Potassium chloride	11·08	10·70	8–14
Sodium chloride	5·68	4·20	4–8
Magnesium chloride	17·65	24·60	15–25
Magnesium sulphate	2·92	1·50	1·5–5
Water	62·67	59·00	
1 cubic metre contained	142·2	140·5 kilo. potassium chloride.	

The crystallising vessels (coolers) are wrought-iron tanks of various sizes, usually from 150 to 300 cubic feet capacity—*e.g.* 7 × 8 × 4 feet. They are best placed a little above the floor, so that the air can circulate underneath, and in summer this should be promoted by Venetian shutters in the building. If the cooling takes place too quickly, the crystals are too small and muddy. Two or three days ought to suffice.

The salt first precipitating carries down such suspended matters as had not been removed by settling; hence such 'bottom salts' are less pure than the 'side salts' crystallising afterwards. The quantity of the latter is sometimes increased by suspending bundles of wire in the coolers, but this is now done but rarely, as the extra labour is hardly recompensed by the advantages of that process. When the cooling has been finished, the mother-liquor is siphoned off, or is run off by a plug, exactly as in the manufacture of soda crystals.

The proportion of bottom salts to side salts ranges from 2 down to 1 part of the former to 1 of the latter; some analyses of this 'first product' run as follows:—

—	Bottom salts		Side salts		Mixtures of both
	Drained	Dry	Drained	Dry	
Potassium chloride	50·2	59·76	60·8	58·31	64–69
Sodium chloride	27·0	32·14	24·4	27·42	28–22
Magnesium chloride	4·3	5·12	2·8	3·15	7·5–8·5
Magnesium sulphate	2·0	2·38	1·0	1·12	0·5–0·5
Insoluble	0·5	0·60	—	—	—
Water	16·0	—	11·0	—	—

The following are analyses of the 'first mother-liquor,' as remaining behind from the 'first product' (I. former process, II. present process):

	I.	II.	
Specific gravity at 20°C.	1·273	1·279	
Potassium chloride	5·50	4·50	p.c.
Sodium chloride	3·80	3·20	„
Magnesium chloride	19·90	22·80	„
Magnesium sulphate	2·70	2·15	„
Water	68·10	67·35	„

Part of it is employed for dissolving fresh crude salts as mentioned above; the remainder is concentrated by evaporation till nearly all the KCl can be obtained on cooling as artificial carnallite. This concentration was formerly carried out in two stages — first to sp.gr. 1·279 (when low-grade potassium chloride was obtained), and then to 1·325; but now, since coal is dearer and lower prices are obtained for the product, it is found best to concentrate at once to 1·325, which means evaporating about one-third of the bulk of the liquor, till the boiling-point reaches 123°C.

The evaporation must be carried on in such manner that the heating surfaces are not covered by crusts of salts, and, of course, in such a way that the fuel is utilised in the best possible manner. Evaporating by means of steam-coils has been found less economical than by means of open fires. Passing over the antiquated modes of concentration as formerly employed at Stassfurt, we shall describe the more recent process. It is now usual to carry on the evaporation successively in two different kinds of apparatus—namely, first, up to the point where salts would be separated in the boiling liquor in ordinary two-flued steam boilers, the steam being utilised for dissolving and other purposes. In lieu of this the first stage is sometimes, and with very great advantage, carried on in combinations of vacuum-pans, such as have been in use for a long time in sugar works, and here and there for caustic liquor. The second stage of concentration, where salts are separated during the process, is best carried on in open pans, heated by internal flues, as shown on a scale of $\frac{1}{75}$ in figs. 4 and 5, which at the same time illustrate the 'step-grates,' universally employed at Stassfurt with the friable brown coal found in the neighbourhood. The flame, generated on the grate *g*, passes through the central wrought-iron tube *a* and back again through the lateral tubes *b b* into the brick flues *l l*. The very strong boiling of the liquor prevents the formation of any crusts of salts on the tubes *a* and *b*.

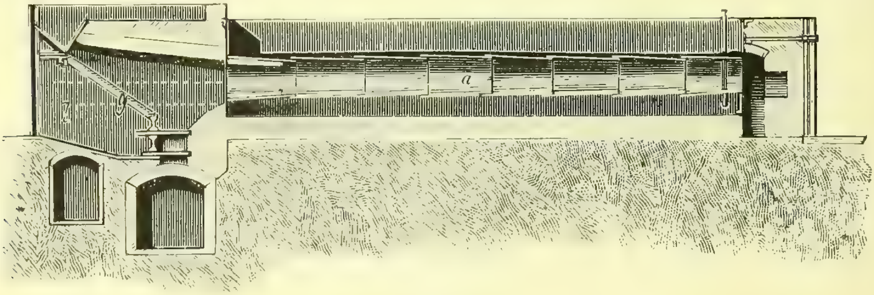


Fig. 4.

During the last few years it has become general to cover in these pans, and to utilise the steam escaping from them in various manners. The consumption of fuel (brown coal) has been greatly diminished by the introduction of gas-producers.

The first stage of evaporation, that in which no salts are separated, ends a little above sp.gr. 1·26; during this time the evaporation is continuous, fresh liquor being run into the boiler to keep it up to the same level. In the second stage the salts were formerly removed by fishing, which might be done more advantageously by mechanical means (compare Thelen's pan, under article Sodium salts). It is, however, usual to boil down to sp.gr. 1·32 or 1·33 in winter, 1·33 or 1·345 in summer (testing the liquor in the muddy and hot state), to allow it an hour's settling, and to run it then into a cooler. The fished salts and the settling mud are washed with water, the washings being utilised for dissolving crude salts; but even then they contain from 7 to 12 p.c. potassium, calculated as chloride, together with 50 to 66 p.c. of sodium chloride, and cause an appreciable loss, as it is not easy to extract that potassium chloride with advantage.

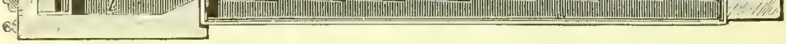


Fig. 5.

The clear liquor contains about 5·5 to 6 KCl, 2–3·3 NaCl, 25–29 $MgCl_2$, 2·6–3 $MgSO_4$, and 59–64 H_2O. It is run into coolers, and left there three or four days. At first—that is, down to a temperature of 65°C.—principally sodium chloride crystallises out, and this can be kept out by a previous cooling down to that temperature. On further cooling 'artificial carnallite' is separated, usually containing from 18 to 22 p.c. KCl, equal to 67–82 p.c. of real carnallite, together with a little NaCl, $MgCl_2$, and $MgSO_4$. This salt is dissolved in water, brought to boiling heat by means of open steam, till the sp.gr. = 1·268 (at 105°C.) has been attained, and a little milk of lime is added at the finish, in order to remove any iron present and to mechanically clear the liquid. The dissolving and settling last an hour each, the subsequent cooling three or four days. The result of the operation is solid potassium chloride, 'second product,' and a 'second mother-liquor,' of sp.gr. 1·257 (measured cold), with 3–4 p.c.

KCl, which is usually added to the 'first mother-liquor' in the concentrating pans.

The quantity of 'second product' amounts to about 20 p.c. of the total make of potassium chloride; its analyses show its comparative purity:

Bottom salts.

—	Drained	Dry
Potassium chloride .	67·0	77·38
Sodium chloride . .	13·7	15·82
Magnesium chloride .	5·3	6·11
Magnesium sulphate .	0·6	0·69
Water . . .	13·4	—

Side salts.

—	Drained	Dry
Potassium chloride . .	80·2	89·02
Sodium chloride . .	7·0	7·77
Magnesium chloride .	2·6	2·88
Magnesium sulphate .	0·3	0·33
Water . . .	9·9	—

The following are tests of the 'final mother-liquor'—*i.e.* that which remains after the crystallisation of the artificial carnallite:

	Former process	Present process
Specific gravity . .	1·319	1·313
Potassium chloride . .	1·25	1·20
Sodium chloride . .	0·95	1·20
Magnesium chloride .	29·50	28·05
Magnesium bromide .	0·30	0·31
Magnesium sulphate .	2·22	3·10
Water	55·78	66·14

Its quantity is 5 or 7 cubic mètres to each 10 tons of crude carnallite, and it is now usually worked for *bromine*; partly also for magnesium chloride (*v. infra*).

Purification of potassium chloride.—This is always performed by washing, utilising the fact that at low temperatures the solubility of KCl decreases very much more than that of NaCl, $MgCl_2$, &c., and that the contact of water with those salts itself causes a lowering of the temperature (sometimes amounting to 10°C.), so that the water in winter would be turned into ice if it were not employed in the tepid state.

The washing of the salt takes place in vessels made of wood or iron, provided with a false bottom, upon which the salt rests. This false bottom is made of wood or of iron plates, perforated with $\frac{3}{8}$-inch holes, and is covered with sacking, or, preferably, with a web of split cane. The water or liquor employed for washing is sprinkled upon the salt by means of an elastic tube, ending in a rose, and the liquor is removed from underneath the false bottom by means of a tap or plug. In fig. 6, A is the tub, *a* a manhole through which the washed salt is removed at the end, *b* the false bottom, *c* the tube and rose for washing, *d* the charging-bogie, *e* the running-off tap.

The tub is completely filled with salt, and this is first washed with washing liquor from a former operation, which in this way yields some of the KCl previously taken up, and takes up NaCl in this stead. After having twice served in this way, the liquor is used for dissolving crude carnallite, in the first operation described above. The first liquor is run off at once, till the mother-liquor has been displaced; the tap *e* is now closed, fresh liquor is run in to the top of the salt, leaving it in contact with the same for two hours, and then running it off. This is repeated with once-used liquor, and last of all with fresh water.

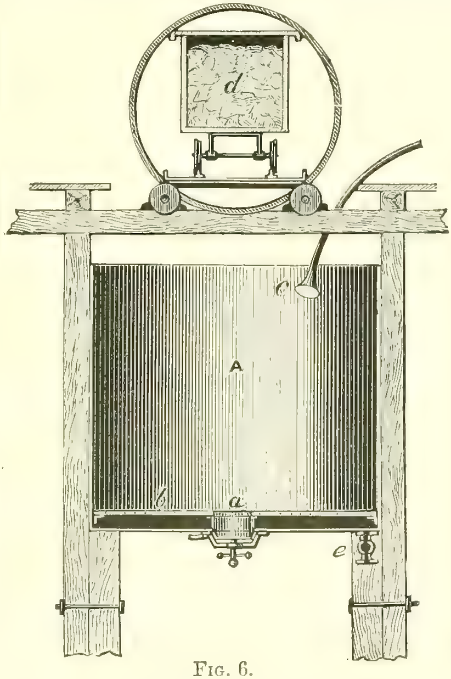


Fig. 6.

The washing operation is not advantageous with products containing less than 50 p.c. KCl; such products are better purified by re-crystallisation.

The following products show the effect of washing on 'first' and 'second' product as formerly obtained:—

I. *First product.*

—	Before washing	Washed once	Washed twice
KCl . . .	52·4	73·4	82·0
NaCl . . .	29·8	22·2	15·3
$MgCl_2$ . .	4·2	1·8	0·5
$MgSO_4$ . .	1·8	0·8	0·4
Insol. . .	0·4	0·3	0·3
H_2O . . .	1·4	1·5	1·5

II. *Second product.*

—	Before washing	Washed once	Washed twice
KCl . . .	79·58	91·25	97·60
NaCl . . .	12·90	6·70	1·25
$MgCl_2$ . .	5·52	0·20	0·12
$MgSO_4$ . .	0·50	0·35	0·20
Insol. . .	0·13	0·15	0·15
H_2O . . .	1·37	1·35	0·68

Washings from I.

—	First liquor	Second liquor
KCl	8·5	11·5
NaCl	15·0	15·3
$MgCl_2$	4·8	1·9
$MgSO_4$	1·2	0·8
H_2O	70·5	70·5

Washings from II.

—	First liquor	Second liquor
KCl	8·17	13·59
NaCl	11·30	11·81
$MgCl_2$	9·87	3·30
$MgSO_4$	0·56	0·20
H_2O	70·10	71·10

The washed salt naturally contains a considerable quantity of water. By simple draining this can be got rid of down to 7 or 9 p.c., by centrifuging to 5 p.c. The remainder is removed by heating, which was formerly mostly done in reverberatory furnaces. The apparatus mostly in use now is shown in fig. 7 on a scale of $\frac{1}{50}$. Upon the foundation *i* a cast-iron drum *h* is mounted, the hollow part of which is heated by steam through *m*, whilst at *n* there is a steam-trap for the removal of the condensed water. In the centre there is a perpendicular shaft *l*, revolving in a bearing protected by a cap. This shaft is moved by means of the pulleys *u* and the bevel wheels *k*, and it carries the horizontal arm *t*, to which are attached a number of plough-shares *a*, a crushing-roll *b*, and a discharging-scraper *c*, set in motion by handle *e* and lever *s*. The last-mentioned part serves at the end of the drying operation for moving the salt towards the circumference, where it falls through an opening, kept shut up to this time, by a slide into a shoot and bag attached to it. Each charge yields 60 kilos. dry salt, and each drying-plate turns out from 2 to 2½ tons per day of 27 hours. With wrought-iron plates of 8 feet diameter, which transmit the heat more easily, nearly 5 tons can be dried in 24 hours. In some places Thelen's mechanical drying-pans (*v.* art. SODIUM SALTS) are employed, which are heated by direct fire, and yield about 15 tons per 27 hours, with an expenditure of 8 to 10 p.c. of brown coal (whose fuel value is not quite one half that of ordinary coal).

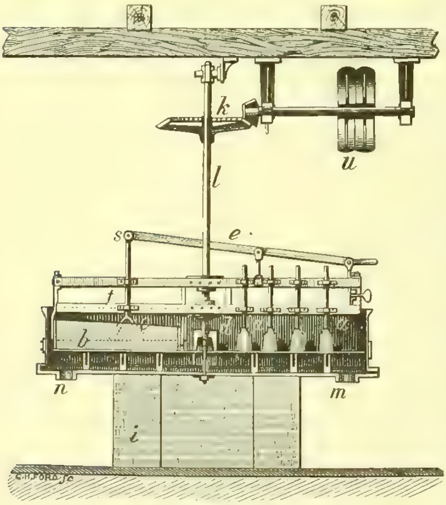


FIG. 7.

Whichever apparatus may be employed, the formation of crusts cannot be entirely avoided. These are removed once a day, and are crushed in order to be sold as manure salts, containing about 70 p.c. KCl.

The drying is usually carried up to 2 p.c. water for low grades, or 0·5 p.c. for high grades; but it is best to leave the salt a short time in a cool, dry place before packing. It is then crushed between rolls, sifted and packed into jute bags, holding 100 kilos. each.

Potassium chloride is sold in strengths of from 75 to 98 p.c., but the price is always calculated upon a basis of 80 p.c. The normal price for 80 p.c. salt is increased for higher strengths, according to a ratio fixed from time to time by a syndicate of the manufacturers; but in all cases the actual weights are reduced to 80 p.c. on the invoice. Thus in June 1885, 100 kilos. of 80 p.c. potassium chloride cost 13 marks 60 pfenn., if the stuff was really only 80 p.c. strong; but of 98 p.c. stuff the 80 p.c. cost 14 marks 50 pfenn. per 100 kilos. Bags are never charged for. Sometimes special conditions are undertaken concerning a maximum of moisture, of magnesia, or of sodium chloride.

Analyses of commercial potassium chloride.

—	*a*	*b*	*c*	*d*	*e*	*f*
KCl	80·85	89·78	82·00	96·5	84·30	98·58
NaCl	16·25	8·10	16·00	2·0	12·98	0·22
$MgCl_2$	0·20	0·10	0·40	0·2	0·19	0·07
$MgSO_4$	0·59	0·33	0·30	0·2	0·10	0·12
$CaSO_4$	0·18	0·27	0·25	0·3	0·22	0·24
Insol.	0·33	0·32	0·15	0·2	0·23	0·31
Water	1·60	1·10	0·90	0·6	1·98	0·46

a and *b* manufactured in 1869, *c* and *d* in 1873, *e* and *f* in 1884.

The production of potassium chloride at Stassfurt, calculated at 80 p.c., amounted to the following quantities (it is restricted by a syndicate of the manufacturers):—

1878	110,760	metr. tons.
1879	92,701	,, ,,
1880	96,831	,, ,,
1881	115,266	,, ,,
1882	153,356	,, ,,
1883	146,200	,, ,,
1884	112,950	,, ,,
1885	107,253	,, ,,
1886	114,136	,, ,,
1887	128,230	,, ,,
1888	142,765	,, ,,
1889	133,957	,, ,,

For manufacturing saltpetre and alum the lower grades (80 to 85 p.c.) are mostly employed, for sulphate, carbonate, and chlorate of potash the higher grades (95 p.c. and upwards).

Of the 97,000 tons of potassium chloride sold in 1885, 43 p.c. was consumed in Germany, 57 p.c. was exported. In Germany the consumption was p.c.: 48·4 for carbonate of potash, 43·8 for saltpetre, 5·4 for alum, &c., 2·4 for agriculture. Of the exported article there was consumed p.c.: 38·6 for saltpetre, 14·3 for bichromate of potash, 8·8 for alum, &c., 38·3 for agriculture.

Yields and costs.—In the very best managed works about 85 p.c. of the potassium chloride contained in the crude carnallite is obtained in a commercial form. The loss of 15 p.c. is distributed as follows:—

By dissolving residue	3·4 p.c.
,, kieserite mud	0·2 ,,
,, press mud	5·0 ,,
,, fished salts	1·2 ,,
,, final liquor	4·8 ,,
unexplained	0·4 ,,

But at other works the loss amounts to 20, 25, or even 30 p.c.

The cost of making 100 kilos. of 80 p.c. potassium chloride in 1886 may be taken as follows:—

	Mks.		Mks.
625 to 675 kilos. crude salt at 1·12 marks	7·00	to	8·10
2·3 to 4 hectol. brown coal at 0·32 mark	0·74	,,	1·28
Wages and salaries of foremen	0·70	,,	1·00
Sundries	0·66	,,	1·00
Total	9·10	,,	11·38

(The 'Sundries' can hardly include bags, interest on capital, depreciation of plant, &c.)

A new process for treating carnallite has been patented by Schliephacke & Riemann (Germ. Pat. 43,922). They smelt raw carnallite in a cupola furnace with felspar or granite, and run the liquid product into cold water, whereby it is granulated and the soluble salts are more easily extracted. Magnesium silicate remains behind in an insoluble state; the solution, which contains the potassium as silicate, is treated with a solution of crude carnallite or waste liquors from the manufacture of potassium chloride. The ensuing reaction is:

$$MgCl_2 + K_2SiO_3 = MgSiO_3 + 2KCl,$$

so that only potassium chloride remains in solution. The gases escaping from the throat of the cupola furnace are to be treated for chlorine and hydrochloric acid. (This ingenious-looking process does not seem to have been practically carried out.)

BY-PRODUCTS OF THE STASSFURT POTASH INDUSTRY.

1. Kieserite. This insoluble body,

$$MgSO_4,H_2O,$$

which becomes soluble only by prolonged contact with water, when it passes over by an intermediate stage into Epsom salts $MgSO_4,7H_2O$, is naturally left behind in the residues from dissolving crude carnallite and settling the liquor. Most of it is lost in the shape of pit heaps &c.; only then it is regularly recovered by the potash manufactures, when they are obliged to get rid of their residues by washing away, because in this case the law compels them to retain the insoluble portions; otherwise kieserite is only prepared when there is special demand for it. Since it soon passes over into the abovementioned intermediate stage, it must be made from fresh residues, which is done by subjecting them to a combined levigating and sifting process. A convenient apparatus for this purpose is shown on a scale of $\frac{1}{50}$ in fig. 8, where *g* is a hopper containing the residues, which rest on a grating; the water issuing from *b* produces a muddy liquor, which meets the slanting sieve *c*; the coarser portions run off at *f*, the finer ones pass through into the slanting shoot *d*, where at first anhydrite is deposited, whilst further on, at *e*, kieserite is found. The clay, together with a little boracite, remains suspended till the last, and is kept back in special settling basins. Of course, in lieu of the slanting shoot *d*, several settling troughs with overflows can be employed.

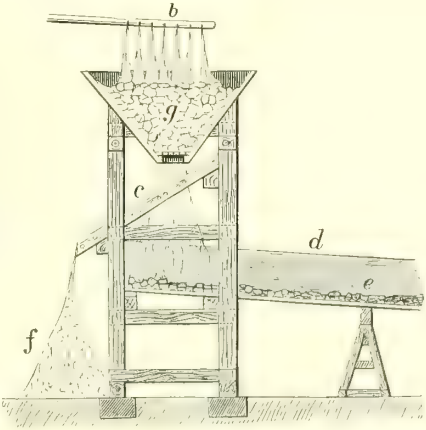


FIG. 8.

The kieserite must be removed in short intervals and put into iron or wooden moulds, where it solidifies after fifteen minutes, so far that the blocks can be taken out. The solidification (which is a process similar to that occurring with gypsum, a chemical combination with water taking place) proceeds with evolution of heat; in a few days the blocks, weighing $\frac{1}{4}$ to $\frac{1}{2}$ cwt., are as hard as stone, and can be sent out in this state without being packed in casks, bags, or the like. After a lapse of time, however, they fall to powder by the attraction of atmospheric moisture and formation of Epsom salts.

The quality of block kieserite naturally varies, according to the more or less careful separation from other matters; a minimum of 60 per cent. magnesium sulphate is frequently guaranteed. When it is required in the ground state, it is first calcined in a reverberatory furnace.

Analyses of kieserite blocks.

—	Fresh		Calcined	
	a	*b*	*a*	*b*
Magnesium sulphate . .	60·20	58·0	81·5	77·8
Sodium chloride .	1·55	2·1	2·1	2·7
Insoluble (anhydrite, &c.) .	10·63	13·5	14·4	17·0
Water. . .	27·62	26·4	2·0	2·5

The yield of block kieserite is about 10 p.c. of the crude carnallite. With careful work it can be got up to 12 p.c., but this is scarcely ever done, because at present only one-tenth of the residues is worked for it, the demand not being equal to the supply.

Applications of kieserite.—Most of it is employed for making Epsom salts, some of it for potassium sulphate. We mention the following attempts at utilising that substance in other ways.

G. Clemm (in 1863) calcined the kieserite, preferably mixed with coal, in the presence of steam, and carried the vapours into vitriol-chambers; magnesia remains behind (in a very impure state). By a similar process Precht (in 1881) makes basic linings for the steel process. Several other inventors have tried to utilise either the sulphuric acid or the magnesia, but hitherto not to any appreciable extent.

The only extensive employment of kieserite is that of converting it into *Epsom salts*, of which about 25,000 tons per annum are made in Germany, and a considerable quantity in England. The process consists simply in causing the kieserite to take up more water, preparing a solution, and allowing this to crystallise. Formerly the process was promoted by calcining the kieserite, after which it is at once soluble in water; but this object can be equally attained by the prolonged application of steam, or, even more cheaply, by soaking the crushed kieserite with the mother-liquor from the Epsom salts, when it gradually passes over into the heptahydrated salt, with great increase of bulk. A solution is now prepared by water and steam, of sp.gr. 1·31 to 1·325 (tested hot and muddy). This is clarified in settlers, where it is kept about an hour, and is then run into iron coolers; if the product is required to be entirely free from iron, the coolers must be lined with lead.

After three or four days the crystallisation is finished; the crystals are all the finer the more concentrated the liquor had been, and they are at first practically free from sodium chloride. By concentrating the mother-liquor inferior qualities are obtained; the last liquor is run to waste.

The crystals of Epsom salts are in England merely drained by a centrifugal machine, turning out two tons per day, and the product, still containing 3 or 5 p.c. of moisture, is directly packed into casks; in Germany they are dried in a room heated by exhaust steam, &c., at a temperature not exceeding 45°C., the dry salt is passed through wooden rollers, leaving a space of $\frac{3}{8}$ inch, so that only the lumps are crushed; it then passes through a sieve, and from this into the casks.

The manufacture of 100 kilos. Epsom salts requires:

125 to 130 kilos. kieserite at 0·70 mark . .	mark	0·86	to	0·91
25 kilos. coal or 0·75–1·0 hectol. brown coal at 0·32 mark.	,,	0·24	,,	0·32
Labour . . .	,,	0·50	,,	1·00
Casks . . .	,,	1·00	,,	1·00
Sundries . . .	,,	0·25	,,	0·50
	,,	2·85		3·73

The principal application of Epsom salts was formerly the medicinal one, which, of course, did not amount to large quantities. At present the greater portion of it is employed in finishing textile fabrics, especially calico. Other applications (mostly only proposed or temporarily tried) are those for replacing the 'pearl-hardening' in paper-making (mixed with lime), for preparing precipitated barium sulphate, for purifying beet-root sugar juice, for rendering fabrics fire-proof, for manufacturing sulphuric anhydride, in several soda-making processes, and so forth.

2. **Glauber's salt** $Na_2SO_4,10H_2O$, can be made by Balard's process—that is, exposing a mixed solution of sodium chloride and magnesium sulphate to a temperature below 0°C., when the following reaction takes place:

$$2NaCl + MgSO_4 + 10H_2O$$
$$= MgCl_2 + Na_2SO_4,10H_2O.$$

The Glauber's salt crystallises out, magnesium chloride remaining in solution. At the mouth of the Rhone this is done by artificial cold; at Stassfurt it can be done without that during the winter months. The material is present in the residues from dissolving crude carnallite, whose composition has been stated on page 269. Just the weathered residue, which is no more adapted for the treatment for kieserite, is most suitable for the above process, and from 50,000 to 75,000 tons of Glauber's salt might thus be made per annum; but the quantity actually produced is only about 10,000 tons, and varies very much according to the favour of the season.

The residue is dissolved in various ways; the longer it has been exposed to the weather, the more easily the solution takes place. Usually the residue heaps are lixiviated on the spot by means of hot water, the solution being caught in a trench made at the bottom of the heap. If the proportion is not $=2NaCl$ to $1MgSO_4$, the composition of the liquor is corrected and its strength is brought up to about 1·269 at 33°C. The solution is clarified by settling, and is exposed to the cold of a winter's night, always under the open sky. Ordinary coolers are not so well adapted to this purpose as large, shallow tanks, made of pine-wood planks, the joints being made tight by caulking with hemp and tar. These tanks are erected on wooden pillars, and are sometimes 100 by 100 feet square, and 8 inches deep. During summer, when they are not used, they are kept filled with a solution of common salt. In such shallow tanks the liquor is better cooled down during the night, 1 cubic mètre often yielding 150 to 180 kilos. of crystals. The mother-liquor is run off in the early morning, before it can get warm again; it shows the sp.gr. 1·205 to 1·225. The processes for obtaining different descriptions of crystals, and for obtaining anhydrous salts, are described in *Sulphate of soda*, art. SODIUM SALTS.

3. **Magnesium chloride** $MgCl_2,6H_2O$, is obtained by evaporating the 'final mother-liquor' to sp.gr. 1·388 or 1·40 (taken hot), allowing to settle for an hour, and running into a cooler, whereupon the whole mass solidifies in a few days. It is broken into large pieces, which are put into casks; the empty space is filled up by a hot, strong solution of magnesium chloride, which, on cooling, cements the whole into a solid mass. Sometimes the dry salt is melted for some time in a furnace, to expel some more water, but if this is driven too far, hydrochloric acid escapes as well. This process is much dearer than the first, and there is not much gained by it. It is preferable to carry on the evaporation from the first to sp.gr. 1·44, and to run the liquid in this state through the bunghole into petroleum casks, in which it solidifies, and is sent out in this state. The analyses show:

	Boiled down to sp.gr. 1·388	Boiled down to sp.gr. 1·44
Magnesium chloride .	45·74	51·05
Potassium chloride .	1·35	1·38
Sodium chloride .	0·25	0·27
Magnesium sulphate	0·15	0·10
Water	52·51	47·20

Since one ton of that product can be obtained from three (or, with care, from 2½) tons of crude carnallite, enormous quantities might be made at Stassfurt; but actually only about 12,000 to 16,000 tons are made, and are principally employed for dressing (lubricating) the warp in weaving calico. A very large number of further applications has been proposed, in order to utilise either the chlorine, or the magnesia, or both. We mention here the following applications: as a disinfectant, for precipitating waste soap-leys; for carbonising wool; for making patent fuel; for magnesia cement; for preparing magnesia, principally as 'basic lining' in the manufacture of steel; for manufacturing barium chloride.

Quantities of magnesium chloride manufactured in

1879 .	8,949 tons	1885 .	11,994 tons
1880 .	11,210 ,,	1886 .	13,062 ,,
1881 .	11,070 ,,	1887 .	12,667 ,,
1882 .	12,446 ,,	1888 .	16,643 ,,
1883 .	19,259 ,,	1889 .	16,728 ,,
1884 .	12,458 ,,		

By far the most important outlet for magnesium chloride would be found in the manufacture of chlorine, if the Pechiney-Weldon process were ultimately successful; this and the other chlorine processes are described in the article on CHLORINE (vol. i. p. 522 *et seq.*). In 1888 that industry had not yet been practically introduced at Stassfurt, but there were preparations made for it. In 1891 hydrochloric acid from this source was coming into the market.

4. **Bromine** is largely made of the final mother-liquor of the Stassfurt works, which contains about 0·25 or 0·29 p.c. of it in the state of $MgBr_2$; *cf.* the article BROMINE.

5. **Boracic acid** is made from boracite or stassfurtite, $2Mg_3B_8O_{15},MgCl_2$, of which about 300 tons per annum is got at Stassfurt. It is dissolved in concentrated hot hydrochloric acid; the clarified solution is run into wooden coolers, lined with lead, where boric acid crystallises out. The crude acid is purified by washing or recrystalling. 100 parts of commercial boracite yield about 82 to 85 parts of crystallised boracic acid H_3BO_3, which is partly sold as such, and partly converted into the sodium salt, known in trade as BORAX (*cf.* this).

6. **Potassic manures** (*artificial fertilisers*) are made from all the by-products of the Stassfurt manufactures, as well as from minerals specially got for this purpose, especially kainite, The manufacturing operations consist merely in grinding, drying, calcining, and effecting a proper mixture to bring the product up to the guaranteed percentage of potash. Potassium sulphate is much better for this purpose than chloride, and magnesium chloride in the free state is absolutely injurious to vegetable life. Hence kainite and schoenite (*cf. Potassium sulphate*) are most usually employed as manures; but low-grade potassium chloride is also frequently sold for this purpose.

In 1888 the production of potassium chloride and the above-named by-products, as well as some other salts, at Stassfurt amounted to about:

140,000	tons	potassium chloride
25,000	,,	manure salts
16,000	,,	potassio-magnesium sulphate
2,000	,,	potassium sulphate for manure
20,000	,,	carbonate of potash
10,000	,,	Glauber's salts
10,000	,,	kieserite
2,500	,,	Epsom salts
17,000	,,	magnesium chloride
400	,,	bromine
120	,,	potassium bromide.

Potassium chloride from the mother-liquors of the manufacture of sea-salt.

The utilisation of the mother-liquors, obtained in the manufacture of sea-salt by voluntary evaporation in the 'salt gardens,' is not generally attempted. It has, however, been worked out to great perfection in at least one locality, at Giraud en Camargue, at the mouth of the Rhone, originally by Balard, later on by Merle and Pechiney. The most recent descriptions of this industry have been given by Wurtz (Hofmann's Bericht über die Wiener Ausstellung, 1875 [1], 410) and Lunge (Chemische Industrie, 1883, 225). We quote here only those portions referring specially to potassium chloride.

From each cubic mètre of sea-water, after obtaining the salt, 64 litres of mother-liquor, testing 27° Baumé, remains behind. This mother-liquor is concentrated by solar heat to 32½°B.; the salt crystallising out during this operation is of inferior quality (down to 91 p.c. NaCl), and is not utilised at all at Giraud. But on further evaporating, by solar heat, from 32·5 to 35° Baumé, a mixture of sodium chloride with nearly its equivalent of magnesium sulphate is separated, which is known as 'sels mixtes,' and is worked up in various ways, especially for Glauber's salts, by artificial cold (p. 276). The liquor of 35°B. is kept during the winter in very large and deep tanks, where the temperature is prevented from falling below 12°C.; in this case only Epsom salt crystallises out, but no carnallite. The new mother-liquor, testing 33°B., of which 16 litres per cubic mètre of sea-water has remained, is further evaporated by artificial heat in a Porion's furnace till it shows 37°B., tested hot. On the other hand, magnesium chloride solution, obtained at a later stage as a by-product, is evaporated in ordinary open pans to 40°B. Both hot liquors are run at the same time into an iron mixing pan, taking care to keep up an excess of magnesium chloride. This causes at once a considerable separation of 'sels mixtes' (*cf.* above), which are removed by a dredging apparatus. The hot liquor remaining behind still contains all the potassium salt; this is, however, separated on cooling in the form of artificial carnallite, owing to the presence of so much magnesium chloride, most of which is left in the cooled-down mother-liquor. This artificial carnallite, being in the state of fine mud, is easily decomposed by agitation with cold water, when magnesium chloride enters into solution and potassium chloride is left behind in the solid state. By systematic washing the latter can be brought up to 82 p.c. KCl.

Interesting and ingenious as this process is (which in reality is much more complicated than would appear from the preceding short description), it cannot very well compete with the Stassfurt industry, based as this is upon the natural accumulation of similar products through thousands of years. Balard's process has hence not made its way elsewhere, and is not likely to do so. At most 400 tons per annum are made in this way.

Potassium chloride from kelp.

In the manufacture of iodine from kelp—that is, the ashes of sea-weed—as obtained on the coasts of Scotland and Normandy, a large quantity of potassium salts is obtained, which, previously to the working of the Stassfurt deposits, was one of the principal sources of these salts for technical purposes. The liquor obtained by lixiviating the kelp is concentrated by evaporation in several stages, and thus yields several crops of crystals. The first crop, called 'plate sulphate,' is a mixture of potassium sulphate with some sodium sulphate and common salt; the mother-liquor yields, on further evaporation while hot, a mixture of common salt with alkaline sulphates and carbonates, which is fished out from the pans and sold as 'kelp salt'; on cooling, a crop of potassium chloride is obtained. The latter can be brought up to upwards of 90 p.c., and formerly about 2,500 or 3,000 tons of it was made per annum; but the development of the Stassfurt industry has mostly compelled the iodine manufacturers to give up the separation of the potassium salts in the pure state, and to utilise the rough mixture of those salts for agricultural purposes.

Potassium chloride from beet-root vinasse.

This product, which always contains potassium sulphate and foreign salts, is described further on, under *Potash from beet-root vinasse.*

Potassium bromide KBr, containing 32·85 K and 67·15 Br, can be made in various ways, always starting from the bromine, obtained in America, in Scotland, or at Stassfurt. Only two of these processes have come into practical use.

The first consists in dissolving bromine in a solution of caustic potash, which ought to be as pure as possible, evaporating the solution, ultimately with addition of a little charcoal, and igniting the mixture. At first the reaction is as follows:

$$6KOH + 6Br = 5KBr + KBrO_3 + 3H_2O.$$

On igniting, the charcoal reduces the bromate to bromide. The mass is dissolved in water, filtered, and the potassium bromide obtained by evaporation and crystallisation.

This process suffers under the drawback that the mass decrepitates strongly on drying, and further losses through volatilisation &c. cannot be avoided. Hence another process is almost exclusively employed now, similar to that used for potassium iodide. A bromide of iron is first prepared, and this is decomposed by potassium carbonate. Some iron bromide is obtained from the first in the manufacture of bromine, the vapours being absorbed by metallic iron, but most of it is made on purpose by mixing bromine and iron in such proportions that the compound Fe_3Br_8 is obtained (*cf. Potassium iodide*). The solution of this bromide is filtered, and is run into a hot concentrated solution of potassium carbonate, till the reaction is exactly neutral or very faintly alkaline. 100 parts of iron bromide require from 56 to 60 parts of potassium carbonate, according to its purity. The solution is boiled for some time, to make the precipitate of hydrated iron oxides more dense; it is then separated from the latter by a filter or filter press, and is evaporated to dryness. The residue is dissolved again, leaving behind the difficultly soluble potassium sulphate &c., and is evaporated for crystallisation. Up to sp.gr. 1·53 this can be done at a boiling heat; the further evaporation should be done at a gentle heat, as with the iodide, to obtain hard crystals. The crystallisation takes place in stoneware or enamelled iron dishes. The mother-liquor can be freed from carbonate by cautious neutralisation with bromhydric acid, and from sulphate by means of barium bromide. Chloride cannot very well be removed from the bromide; hence the bromine employed should be as free from chlorine as is required. Iodide can be removed by boiling with bromine. The last mother-liquors are best used up for the recovery of bromine. The German Pharmacopœia permits the presence of 2 p.c. KCl and 0·1 p.c. K_2CO_3 in potassium bromide.

The drying of the potassium bromide takes place at 40° or 50°C., not above (to avoid decrepitation), on plates of stoneware or of sheet-iron covered with a very hard lacquer or with enamel.

The German manufacture of potassium bromide amounts to about 120 tons per annum, half of which is made at Schering's works at Berlin. A similar or larger quantity is made in

America, and much more could be obtained if there were demand for it.

The application of potassium bromide is restricted to medicine and photography.

Potassium iodide KI, containing 23·95 K and 76·05 I.

There are many ways for preparing this salt, but only the following processes are used for manufacturing purposes.

1. *By means of caustic potash.* The reaction is, $6KOH + 6I = 5KI + KIO_3 + 3H_2O$. The potassium iodate on igniting yields up its oxygen and is converted into iodide, but as losses are caused by decrepitation and volatilisation, it is preferred to add some carbon in order to reduce the iodate.

The caustic potash ought to be as pure as possible; most of the impurities of commercial potash would enter into the iodide, and could not be removed from it by crystallisation, owing to the great solubility of the iodide. Hence it is preferable to start with the purest procurable potassium carbonate, such as is supplied in the crystallised form to flint-glass makers, or that made by calcining potassium bicarbonate. The carbonate is causticised in the usual manner, employing pure lime, and iodine is introduced in small quantities into the boiling liquor till it has been exactly neutralised. The solution is evaporated to dryness, adding to it in the syrupy state some lampblack or charcoal, previously treated with hydrochloric acid and thoroughly washed with water, to the amount of $\frac{1}{25}$ of the iodine present. The dry mass is gradually introduced into an iron pot, heated to redness, where it is brought to fusion, keeping the pot covered in order to prevent the iodide from volatilising. When completely fused, the mass is ladled out and is dissolved in water; the solution is filtered and is evaporated to about 1·82, when it crystallises on cooling. The evaporation is best done by heating the solution in porcelain dishes on a sandbath, but not to boiling heat, the more concentrated liquors being farthest from the fire-end. A hood protects each dish from dust, draught, &c. In this way very good crystals are obtained.

The crystals, after draining, are dried on enamelled or lacquered iron plates in a current of hot air. If the salt is required to have an opaque appearance, the temperature is ultimately raised to 120° or 130°C.

2. *By means of iron.* A solution of ferrous iodide is prepared by digesting 3 parts of iodine with 1 part of iron borings and about 8 of water. The solution is filtered and one-third of the original quantity of iodine is dissolved in it with the aid of heat, so that it now contains a ferroso-ferric iodide, Fe_3I_8. This solution is now mixed in a porcelain or enamelled iron vessel with a boiling solution of pure potassium carbonate, and the boiling is continued till the precipitate of ferroso-ferric oxide has become dense, whereupon it is separated from the solution of potassium iodide by filtration. The reaction is:

$$Fe_3I_8 + 4K_2CO_3 = 8KI + Fe_3O_4 + 4CO_2.$$

The following modification, by Liebig, dispenses with the slow solution of iodine in ferrous iodide, and the troublesome frothing in the last reaction, owing to the escape of carbon dioxide. A solution is made of 12 parts iodine, 3 iron, and 32 water; to this is added, without previous filtration, a solution of 6 parts iodine in 12 parts caustic potash liquor of sp.gr. 1·345, and ultimately 9 parts of the same caustic liquor. The mixture is boiled for some time, filtered, evaporated to dryness, whereby a little ferric hydroxide is separated, re-dissolved, filtered and brought to crystallisation as above. The product is extremely pure, free from iodate, and the yield almost the theoretical one.

3. *By means of cuprous iodide.* Sometimes considerable quantities of cuprous iodide, containing from 60 to 66 p.c. of iodine, are shipped from Peru. This is converted into potassium iodide by washing it, suspending it in water acidulated with a little sulphuric acid, passing in sulphuretted hydrogen till all the copper has been precipitated, adding enough solution of iodine in potassium iodide to destroy the excess of H_2S, separating the solution of iodhydric acid (containing a little finely-divided sulphur) from the precipitate, neutralising it with potassium bicarbonate, evaporating, separating the sulphur which has now become globular, and bringing to crystallisation.

Nearly all the potassium iodide manufactured is employed in medicine and for photographical purposes. For the former purpose it is required to be entirely free from chloride.

Potassium sulphate K_2SO_4 is obtained as a by-product in several manufactures which are described elsewhere; thus, in the working up of beet-root vinasse (*cf. Potassium carbonate*, p. 289), and in that of kelp, where it is separated as 'plate sulphate,' containing from 76–83 p.c. K_2SO_4, with 9–21 p.c. Na_2SO_4, some KCl and other salts (p. 278). It is further contained in the ashes of plants, and is hence present in commercial potashes; on purifying these it is obtained as a by-product, easily separable from the carbonate on account of the great difference in solubility.

The bulk of the potassium sulphate found in trade is, however, either made from kainite, or by the decomposition of potassium chloride with sulphuric acid.

Very large quantities of potassium sulphate are found at Stassfurt and Kalusz; not, however, in the isolated form, but principally in that of *kainite* $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, always mixed with sodium chloride, calcium sulphate &c., so that commercial kainite contains at most 70 p.c. of the pure mineral. A very large number of processes have been invented for preparing potassium sulphate, either from kainite or from mixtures of magnesium sulphate (in the shape of kieserite) and potassium chloride or carnallite. In most cases an intermediate product is made, the magnesium-potassium sulphate, $K_2SO_4,MgSO_4,6H_2O$, which occasionally occurs among the Stassfurt minerals, and has received the name of 'schoenite.' From this potassium sulphate is prepared with comparative facility, but at present it hardly pays to do so, at least in a sufficiently pure state for the manufacture of potassium carbonate; hence nearly all the latter is made from sulphate, obtained, with potassium chloride and sulphuric acid (see below), or from vinasse, while the schoenite is sold as a fertiliser.

In 1888 the daily consumption of kainite for conversion into schoenite or sulphate was from 175 to 200 tons.

We give here a short synopsis of the more important processes, which are described in more detail in Pfeiffer's 'Kali-Industrie' (Braunschweig, 1887), p. 349 *et seq.* The figures put in brackets are the numbers of the German patents.

1. *Preparation of schoenite from kainite.* Borsche & Brünjes (10,642, 11,028, 10,701, 12,875, 17,795) prepare a cold saturated solution of kainite and employ this for extracting fresh kainite at a temperature of 80°. The solution, which shows the sp.gr. 1·337, is clarified, and on cooling yields a crop of schoenite; the mother-liquors, which are rich in magnesium and sodium and potassium chloride, generally enter into the manufacture of potassium chloride from carnallite. This process is actually at work on a large scale.

Dupré & Hake (6,053) treat finely-ground kainite with a cold saturated solution of magnesium sulphate, at 20° or 25°C.; this carries away magnesium and sodium chloride, together with one-third of the potash, two-thirds of the latter remaining behind as schoenite. The dissolved 33 p.c. of potash is also partially recovered. This process is also at work, but not on a very large scale; the employment of magnesium sulphate makes it rather more expensive than the preceding one.

H. and R. Grüneberg (10,754, 18,947) extract the kainite by a hot solution of schoenite or of sodium chloride; on cooling schoenite crystallises out.

Precht (10,637, 13,421, 19,456) treats kainite with water or previous liquors at 120–145°C., under a steam-pressure of 2–7 atmospheres, with mechanical stirring, in a very ingeniously-constructed apparatus, which permits a mechanical separation of the double salt formed from the solution and from the residual rock-salt. The double salt formed in this way has the formula $K_2SO_4,2MgSO_4,H_2O$, and is converted into schoenite by agitation with a small quantity of water. This process is also at work on a large scale.

Similar processes are those of Loefasz (29,223) and Nahnsen (10,772, 24,744).

Dupré (53,237) works up mixtures of kainite and sylvinite ($75KCl+25NaCl$) by treating them with a hot solution of kainite, when almost pure $K_2SO_4,MgSO_4,6H_2O$ crystallises out.

The Westeregeln alkali works (50,596) boil ground kainite with the last mother-liquor from the manufacture of potassium chloride, containing 30 p.c. $MgCl_2$, thus producing various salts.

The schoenite thus obtained, which is entirely used for agricultural purposes, has the following average composition:

Potassium sulphate	48 to 52 p.c.
Magnesium sulphate	32 „ 36 „
Water	3 „ 12 „
Sodium chloride	1 „ 5 „
Gypsum and insoluble parts	0·2 „ 5 „

Several processes for preparing schoenite from potassium chloride or carnallite and kieserite (Brünjes, 11; Ferber, 5,068; Grüneberg, 5,607; Westeregeln, 27,404) need not be described here, because this does not seem to be profitable. The principal reaction taking place is:

$$2MgSO_4+2KCl=K_2SO_4,MgSO_4+MgCl_2;$$

or better

$$4MgSO_4+6KCl=2K_2SO_4,MgSO_4+2KCl,MgCl_2.$$

Special processes for recovering schoenite from waste liquors are those of R. Grüneberg (10,753), Bernhardi (10,821, 12,493), Vorster and Grüneberg (28,772).

It is now a fixed rule of trade that 'crystallised' potassio-magnesium sulphate is to contain 41 or 42 p.c. 'calcined,' 48 or 50 p.c. real potassium sulphate. In 1888 the prices of those articles were Mk. 7 resp. Mk. 8·50 pro 100 kilos.

Quantities of potassio-magnesium sulphate made at Stassfurt in

1883	13,037 tons	1887	24,082 tons
1884	25,765 „	1888	11,478 „
1885	27,207 „	1889	16,325 „
1886	29,045 „		

2. *Preparation of potassium sulphate from schoenite.* This can be done by simply running a saturated hot solution of schoenite upon dry powdered potassium chloride. The reaction theoretically is:—

$$K_2SO_4,MgSO_4+3KCl=2K_2SO_4+KCl,MgCl_2,$$

but practically twice the theoretical quantity of schoenite must be taken, half of which remains in solution. The potassium chloride is rapidly changed into sulphate, and this is separated from the liquor by centrifugal force, taking care that the temperature does not fall below 40°C. Below this temperature, first potassium chloride, then schoenite, and at last carnallite, crystallise out. The reaction can also be brought about by digesting crystallised schoenite with a cold saturated solution of potassium chloride, best of all in a set of vessels methodically combined with one another (Precht's patent, 14,534).

Schoenite, or a mixture of potassium chloride and magnesium sulphate, can be also converted into potassium sulphate by heat. Superheated steam (Sprenger's patent, 27,965) acts only very partially, but the addition of carbon (in the shape of small coal, brown coal, &c.) causes the reaction to proceed to its end by somewhat complicated stages (Precht, 15,747; Leopoldshaller Fabriken, 31,148). Townsend (10,641, 29,307) heats a mixture of potassium chloride, magnesium sulphate, and aluminium silicate in a muffle furnace in the presence of steam. This method has been further worked out by the 'Ascherslebener Werk,' in 1885, and seems to be successful. Hans Müller ignites the mixture of KCl and $MgSO_4$ with ferric oxide (32,325). Dupré and Hake produce, by means of lime or gypsum, a double sulphate of potassium and calcium, which is decomposed by igniting or by redissolving (8,021).

Nearly all the potassium sulphate made from schoenite &c. is used for agricultural purposes.

3. *Preparation of potassium sulphate by decomposing potassium chloride with sulphuric acid.* This process, altogether analogous to the first stage of the Leblanc soda process, was first carried out by Messrs. Vorster and Grüneberg in 1863, near Cologne, and in 1868 at Stassfurt. About the same time (1864–1869) it was introduced in North Germany, France, and England. This way of producing potassium sulphate is nearly always employed when the product has to be converted into carbonate.

The raw materials are (1) potassium chloride of high strength of the Stassfurt manufacture, or, as far as it goes, that from the working up of vinasse which already contains from 8 to 12 p.c. of sulphate, together with a little carbonate (p. 289). Coarse-grained salt is preferred to muddy or lumpy salt. (2) Sulphuric acid of sp.gr. 1·67, generally made at the same works. This is a lower strength than that preferred for decomposing sodium chloride, where the reaction is not so violent.

The decomposition of potassium chloride is so closely akin to that of sodium chloride that we can refer in most respects to the article SODIUM SALTS. The furnaces, acid condensers, &c., are the same in both cases. We must, however, make the following remarks concerning some peculiarities of the potash industry.

The 'decomposing pans' (pots) are exactly similar to those used for common salt, so are the furnaces, of which all three descriptions, as employed for common salt, are in use here as well. But while in the case of sodium chloride the 'close,' or muffle furnaces are considered the best, owing to the better condensation of hydrochloric acid, many potash manufacturers prefer 'open'—that is, reverberatory—furnaces, a higher temperature being required for decomposing potassium sulphate and the work being done much more quickly (by one-third). Undoubtedly the best furnace for this work is Mactear's continuous revolving furnace (*cf.* SODIUM SALTS), as used at Kalk near Cologne.

The ordinary decomposing pans, which in England produce from 1,500 to 2,000 tons of salt cake before they are worn out, serve only for half or two-thirds that quantity with potassium chloride. At Stassfurt they employ thin pans, 2½ inches thick throughout, which last only for 250 to 500 tons of potassium sulphate. Blügel's firebrick pans (Germ. Pat. 4,207) do not seem to have answered.

The charges are from 5 to 10 cwt. of potassium chloride, and the corresponding quantity of sulphuric acid, which must be varied according to the varying strength of the chloride. That from the vinasse works contains carbonate, which must be taken in account. With muffle furnaces the work is considered sufficiently good if 1 to 2 p.c. KCl and 2 to 3 p.c. 'free' SO_3 is left in the sulphate. Each charge takes about an hour to finish.

With reverberatory furnaces the undecomposed KCl is only 0·5 to 1·5 p.c.; the 'free' SO_3 1 to 2 p.c.

With Mactear's furnace the Kalk works produce from 22½ to 25 tons of potassium sulphate in 24 hours; the product contains only 0, 7 to 1·0 p.c. KCl, and as much free SO_3 (that is, bisulphate). The condensation of the hydrochloric acid is very good, 95 p.c. of the theoretical quantity being recovered.

Theoretically 100 parts K_2SO_4 require 85·6 of pure KCl (corresponding to a yield of 116·8 of the former from 100 KCl), and 45·91 of SO_3 = 75·27 acid of sp.gr. 1·67; and the HCl escaping should be 41·84 parts = 138 parts hydrochloric acid of 32½ p.c. Practically with hand-furnaces 3·5 to 5 p.c., with mechanical furnaces 1 p.c., excess of sulphuric acid must be taken, or even more, if a minimum of undecomposed KCl has to be guaranteed.

The yield of sulphate is almost equal to theory, the small unavoidable loss being made up by matter mechanically taken up from the furnace, flue-dust, &c. The quality has been mentioned above.

The following is an analysis of good commercial sulphate made from 98 p.c. potassium chloride:

K_2SO_4 . .	95·00 p.c.	SO_4H_2 . . .	1·84 p.c.
Na_2SO_4 .	0·50 „	CaO, Al_2O_3, Fe_2O_3	0·81 „
KCl . .	1·50 „	Insoluble .	0·35 „

The yield of hydrochloric acid is usually only 70 to 75 p.c. of the theoretical one with reverberatory furnaces, 90 p.c. and upwards with muffle furnaces or the Jones and Walsh furnace, 95 p.c. with Mactear's continuous furnace.

The wages per ton of sulphate are from 6·5 to 7·2 marks (including the condensation of hydrochloric acid) for hand furnaces, but only one-half or even less for Mactear's furnace.

The fuel used amounts to 9 cwt. of good Westphalian coal with muffle furnaces, or 4 to 5 cwt. coke and 3 cwt. coal for reverberatory furnaces. With Mactear furnaces there is no saving of fuel, since it is necessary to provide steam for the engine turning the furnace.

It was formerly usual to contract for the decomposition of potassium chloride in the following way. For 100 kilos. of chloride supplied 115 sulphate had to be delivered, against a payment of 9 marks, of which 5·5 marks was reckoned as cost of sulphuric acid, 3 marks for various expenses, and 0·5 marks as profit (apart from the hydrochloric acid). Nowadays, the sulphuric acid should cost much less than the above.

The quantity of potassium sulphate made in Germany amounted to in

1879 .	15,749 tons	1885 .	18,149 tons
1880 .	10,602 „	1886 .	17,246 „
1881 .	13,280 „	1887 .	25,365 „
1882 .	18,810 „	1888 .	33,412 „
1883 .	16,201 „	1889 .	29,709 „
1884 .	12,495 „		

Potassium carbonate. Impure potassium carbonate, commercial 'pot-ashes,' has been known in very ancient times. Aristotle mentions its preparation by the incineration of rushes, Dioscorides by that of argol, but only Kunkel, in the seventeenth century of our era, proved the identity of these two products. The Romans employed them in medicine and for soap-making; the latter is even now the most important outlet for that article, as soft soap cannot be made with soda. Otherwise soda tends more and more to displace the more expensive alkali potash, and has done so in the manufacture of hard soap, in that of glass (partially even in that of flint glass and Bohemian crystal), and more recently, to some extent, even in some manufactures which formerly seemed to be exclusively possible with the use of potash, as that of chromates, chlorates, and ferrocyanides. In the manufacture of oxalic acid from sawdust caustic potash is also considered indispensable.

Leaving aside such methods as cannot be classed among manufacturing processes (such as the incineration of argol or wine-lees) with or without potassium nitrate, we may enumerate the following commercial sources of potassium carbonate:—

1. *Mineral.* (*a*) From potassium chloride and sulphate by Leblanc's or other processes.

(*b*) From felspar and other rocks containing potash.

2. *Vegetable.* (*a*) From wood ashes.

(*b*) From beet-root molasses (vinasse).

(*c*) From kelp or varech (very unimportant).

3. *Animal.* From the 'suint' of sheep's wool.

Potassium carbonate (or caustic potash) manufactured from the chloride or sulphate. All processes starting from this base are of very recent date, and only that imitating the Leblanc soda process has acquired great importance. In 1861 Messrs. Vorster and Grüneberg, of Kalk, near Cologne, commenced working up potassium sulphate (which at that period was a by-product in working up vinasse cinder, less valuable than chloride, and difficult to get rid of) by the Leblanc process, and this industry has gradually spread over other parts of Germany, which is the principal seat of that industry. In England the Leblanc process seems to have been attempted with potash about 1863 or 1864, but it was only somewhat later employed for making commercial carbonate, and has not gained any great extension there. In France it was introduced in 1873, at Croix, near Lille, and to other works in the North.

We shall now enumerate the principal processes for manufacturing potassium carbonate from chloride or sulphate, omitting those which have been originally proposed for soda without special adaptation to potash (*v.* Sodium salts):—

(1) *From chloride, without passing through sulphate.* The *ammonia* process, which is of such importance for the manufacture of soda (comp. this) is not applicable to potash, because the solubility of potassium bicarbonate is too great. An attempt to overcome this by working in an alcoholic solution, by Grousilliers (Germ. Pat. 10,552) was entirely unsuccessful.

A very ingenious process is that of Ortlieb (Germ. Pat. 5,786, 9,376, and 13,397), replacing ammonia by *trimethylamine*, which is obtained by a certain treatment of beet-root vinasse (*cf.* below). The great solubility of trimethylamine hydrochloride admits of separating the potassium bicarbonate; cold pressure and agitation promote this object. The reaction is hence:—

$$\mathrm{KCl + N(CH_3)_3 + CO_2 + H_2O}$$
$$\mathrm{= KHCO_3 + N(CH_3)_3.HCl.}$$

The limited supply of the reagent, its high price, its extremely unpleasant smell, are drawbacks to this process, which otherwise seems to have worked well in the experimental factory at Croix, where it was, however, given up again after a short time.

Engel patented the following process (Germ. Pat. 15,218):—Suspending *magnesia* or natural magnesite in a solution of potassium chloride, and passing in carbonic acid under pressure, when a double carbonate of potassium and magnesium is precipitated, which can be decomposed into the single salts by heating or dissolving in water:

$$\mathrm{3MgCO_3 + 2KCl + CO_2 + H_2O}$$
$$\mathrm{= 2MgCO_3,KHCO_3 + MgCl_2.}$$

The recovery of magnesia from the chloride would have presented difficulties, but there must have been others as well, for the works started at Stassfurt were soon stopped again. Delsol (39,903) patented an addition to Engel's process.

A further patent of the Salzbergwerke Neu-Stassfurt (Germ. Pat. 50,786) describes an improved process for treating the compound $\mathrm{KHCO_3,MgCO_3,4H_2O}$ with water under pressure at 140°. In 1891 the process was still at work, but its success not yet assured.

In 1885, Borsche and Brünjes patented the production of carbonate from chloride or sulphate by means of ammonio-magnesium carbonate and carbon dioxide. This process was to be actually carried out on a large scale, with what success is still an open question.

Wittjen and Cuno (Germ. Pat. 19,197) employ *zinc* in lieu of magnesium compounds for a similar process.

Scheele's process, treating an alkaline chloride by *litharge*, has been repeatedly attempted without practical success. It has been applied to potash by the Société anonyme Lorraine industrielle (Germ. Pat. 23,701), and by D. C. Knab.

Gilchrist Thomas (Germ. Pat. 30,209) treats alkaline chlorides in the shape of blocks in a heated converter with *pig iron*, containing little carbon, but upwards of 4 p.c. silicium, in a stream of hot air and superheated steam.

Wagner, in 1865, proposed precipitating potash by *hydrofluosilicic acid*, and decomposing the potassium fluosilicate by lime.

Several inventors utilise the slight solubility of potassium *bitartrate* (Goldenberg) and *binoxalate*. Bohlig decomposes the latter by magnesium carbonate. None of these processes are practicable.

The decomposition of alkaline chlorides by the *galvanic current* has been frequently attempted. This process has been applied to carnallite by Wollheim (Germ. Pat. 16,126); at Aschersleben it was to be tried on a large scale with machines of 120 h.-p. The Griesheim Chemical Company at Frankfort have carried out the electrolytical manufacture of caustic potash and chlorine from strong potassium chloride with great success, and on a very large scale, for some years past, but it is not known by what special process.

(2) *From sulphate.* Leblanc's process will be described below. It has been extended to a direct treatment of *schoenite* by Vorster & Grüneberg, and Precht (in 1885) even patented a direct addition of magnesium sulphate. Clemm (1863) and Precht (1885) decompose schoenite by heating with *coal*, whereupon a mixture of magnesia and potassium sulphide is formed, which is treated with moist carbon dioxide.

The processes in which compounds of barium, strontium, aluminium, &c., also aluminium phosphate, are employed for decomposing alkaline sulphates are enumerated *sub* Sodium salts. We mention only the process of Jannasch (Germ. Pat. 51,224), who boils potassium sulphate, obtained by a special process from kainite, with finely ground native barium carbonate (witherite). As he employs the native mineral and no carbonic acid, the decomposition is sure to be incomplete.

E. Pfeiffer states (Z. 8, 1338, 1375) that he decomposed, for some time, potassium sulphate with barium carbonate on a large scale. W. Bramley has patented the same process in a little modified form (Eng. Pat. 1,050, 1886).

Dupré (Germ. Pat. 47,037) mixes solutions, saturated at 0°, of equivalent quantities of potassium sulphate and sodium carbonate (containing 85 grms. Na_2CO_3 and 139 grms. K_2SO_4 per litre), and cools down very cautiously below 0°, passing a stream of CO_2 into the liquid; or else 140 grms. sodium bi-carbonate + 140 grms. potassium sulphate, dissolved in 1 litre water, are cooled down to −6°, when 200 grms. of Glauber's salts crystallise out, which are separated from the solution of potassium bicarbonate by a centrifugal machine. At −10° the separation of Glauber's salts is more complete, but then the process is interfered with by the formation of cryohydrates. A further patent (Germ. Pat. 52,163) contains important improvements of the process.

Vogt and Figge (Germ. Pat. 31,675) convert alkaline sulphates into a porous form by mixing them with silica, clay, magnesia, or lime, calcining, and moulding into small pieces. These are introduced into upright iron cylinders, in which the sulphate is first converted into sulphide by the action of carbon monoxide at a bright-red heat, carbon dioxide being given off, and then into carbonate by the action of carbon dioxide and steam at a lower temperature. These cylinders are combined to a set, in which carbon monoxide is passed in at one end and hydrogen sulphide passes out at the other end. The cylinders are discharged from the bottom; the mass is lixiviated, and the porous substance employed over again. This process was to be tried on a large scale at the Aschersleben works; it does not seem to have been successful.

Kayser (Am. Pat. 320,256) converts alkaline sulphates into carbonates by a mixture of equal volumes of CO_2 and CO at a low red heat; SO_2 escapes, and is utilised for converting chloride into sulphate.

Carbonate of potash by the Leblanc process.

This process consists in fusing potassium sulphate with calcium carbonate and coal. Both the theory and the practical execution of this process are exactly like its original application to soda, to which we must refer for particulars. This also holds good of the furnaces, lixiviating apparatus, boiling-down pans, &c. We shall here point out only those matters in which the potash process differs from the soda process.

The potassium sulphate is nearly always that obtained by decomposing potassium chloride with sulphuric acid. That obtained from schoenite (*cf.* p. 280) is too light, and is easily carried away by the draught. Without damaging the process, some schoenite may be mixed with the K_2SO_4.

The *furnaces* are almost exactly like black-ash furnaces; the only difference is that the hearth is made a little 'dished'—that is, with a depression of 2 inches in the centre—to counteract the tendency of the melting mass to penetrate into the hearth and raise it up.

The usual mixture is: 100 potassium sulphate, 80 to 90 limestone, and 40 to 50 coal; but in starting a new furnace the proportion of limestone and coal is somewhat increased till the furnace has attained its full heat. Small batches (of 2½ to 3 cwt. sulphate) are finished in forty to fifty minutes, large batches (up to 5 cwt. sulphate) in about seventy-five minutes, so that there is no advantage with the latter; on the contrary, small batches are more easily worked, and the furnace suffers less; there is also less volatilisation of potassium compounds. Usually thirty batches of 3 cwt., or thirty-five of 2½ cwt., of sulphate are turned out in twenty-four hours.

Towards the end of the operation the fusing mass becomes thinner than with soda; the end of the operation is at hand when the evolution of 'candles' begins to diminish slightly, whereupon the batch must be drawn out at once. The temperature rises from 700° in the beginning to 900°C. in the end.

Good black ash from potash should contain 40 to 45 p.c. potassium carbonate (counting the hydrate as well as such), and not above 0·5 to 1·5 undecomposed sulphate, and 0·5 to at most 1·0 sulphide. It contains all the less caustic, the less limestone and coal are used in the original measure. Cyanide is formed from the nitrogen of the coal, sometimes to such an extent that the recovery of ferrocyanide is a paying process. German coal yields less cyanide than English (Newcastle) coal.

100 parts of potassium sulphate, with an average proportion of limestone, yield from 157 to 163 parts of black ash.

The black ash is left to cool for one or two days, and is broken up in smaller pieces than with soda (say, not above 4 inches diameter). The lixiviation takes place precisely as with soda. For each ton of black ash to be lixiviated in twenty-four hours there should be vat space amounting to from 250 to 350 cubic feet. The water is used in summer without heating; in winter about 30°C.; the 'strong vat' should be at about 40° to 45°C. The strong liquor, as it is run off, tests from 36° to 60°Tw.; the average is 42°Tw. It is greenish-yellow, sometimes with a reddish cast. It contains all the same impurities as soda tank-liquor. Pfeiffer quotes the following quantities found in two samples, calculated upon 100 parts of K_2CO_3 (+KOH):

	a	*b*	
Potassium sulphate .	3·27	4·34	parts
,, sulphide .	3·17	2·35	,,
,, thiosulphate .	1·72	3·61	,,
,, silicate .	1·98	2·24	,,
Total sulphur (as K_2SO_4)	9·6	11·36	,,

There is also aluminate, ferrocyanide, ferrosulphide, &c. The *tank-waste* ought not to contain above 0·2 to 0·3 p.c. of soluble potassium carbonate.

By directly evaporating the tank-liquor to dryness, and calcining, a yellow or reddish potash is obtained which must be purified by redissolving, bringing again to dryness, and calcining. It is decidedly preferable to *carbonate* the tank-liquors exactly as this is done with soda liquors, whereby the hydrate and sulphide are converted into carbonate, and the ferrous sulphide is precipitated. This can be done by gaseous carbon dioxide in the manner described for soda, or very advantageously with potassium bicarbonate.

The *evaporation* of the liquor takes place in pans heated by the waste fire of the black-ash furnace either from the top or the bottom. Pans fired from the top suffer less, and the evaporation takes place more quickly than with bottom heat, which requires about twice the heating surface; still, bottom-fired pans are generally preferred in potash works, because the liquors are less contaminated with SO_2, soot, coal-ashes, &c.

The evaporation can be carried on with good liquors to 77°Tw. before any sulphate 'salts out.' At this point the liquor is run off into coolers, where most of the sulphate is precipitated in a muddy form, together with a little $K_2CO_3 2H_2O$. With inferior liquors, containing much sulphate, this may 'salt out' even at 60°Tw., and this takes place in any case above 77°Tw. up to 123°Tw., at which point all the sulphate will have been removed. That part which is precipitated in the pans during evaporation would, in bottom-fired pans, produce very inconvenient crust unless it were constantly removed by 'fishing.' This can be done most conveniently with boat-pans or with Thelen's mechanical fishing-pans (described in art. SODIUM SALTS). In the case of top-fired pans such deposits are harmless, and hence at some works they employ bottom-heat up to 77°Tw., and top-heat above that point.

The potassium sulphate, precipitated both in the pans and by cooling the liquor, is drained, freed from adhering liquor by cold water, and used over again in the black-ash furnace; this is an advantage against the Leblanc soda process, where the sulphate remains with the soda-ash, and is thus lost. With coal containing much nitrogen it pays to extract the potassium ferrocyanide, which is found together with the sulphate. The deposit is for this purpose dissolved with water and steam to sp.gr. 66½°Tw.; the solution is clarified and run into coolers, where the ferrocyanide crystallises out. It is purified by re-dissolving to 60°Tw. The yield is generally below 1 p.c. of the carbonate.

The *finishing operation* takes place in a calcining furnace, like those employed for soda, but always connected with a cast-iron pot or a wrought-iron pan, set at the end opposite the fireplace, for utilising the waste heat. In those pans the liquor is brought to at least 123°Tw., but sometimes to the state of paste. In the latter case the furnace-bed is made level; when intended for liquor of 123°Tw. it must be made to slope down from the working-door to a depth of 5 or 6 inches. In any case the furnace must be brought to a bright-red heat before charging it with fresh liquor or paste, so that a crust is formed at once on the bottom, and there is less tendency for the liquor to penetrate into the furnace-bed, which, of course, must be made with the greatest care, exactly like that of a black-ash furnace. The new crusts forming at the surface must be worked down, and when the whole mass is dry it must be detached from the brickwork and broken up by means of the 'rake' and the 'paddle.' In the intervals of working the mass the heat is raised by closing the door and stirring the fire till the surface shows just incipient fusion, but not above this point. When the mass has been brought to a red heat throughout, and into the state of a uniform powder, it is drawn out and is left to cool on an iron plate. With liquor of 123°Tw., four or five batches of 5 or 6 cwt. of potash can be turned out in twenty-four hours. It is important to avoid any interruptions of work, which nearly always produce cracks in the brickwork.

With carbonated liquors a single calcination furnishes a marketable product containing 85 to 92 p.c. carbonate, 10 to 2 sulphate, 2·5 to 0·5 chloride, and a little insoluble matter. This is, however, frequently *refined* by redissolving it with the aid of steam, in tanks provided with a suspended sieve or with a mechanical stirrer, to a strength of 110° or 112°Tw., and allowing it to settle, when, on cooling, most of the sulphate crystallises out. The clear liquor is further concentrated to 123°Tw. in the pans behind the calcining furnaces, and is calcined with special care. This refined product contains:

Potassium carbonate (hydrate, silicate, aluminate)	from 92	to 98·5 p.c.
Sodium carbonate .	„ 2·5	„ 0·5 „
Potassium chloride .	„ 2·5	„ 0·6 „
Potassium sulphate .	„ 3·0	„ 0·4 „

The quantity of silicate and aluminate is very slight. Phosphate, which always occurs in potash from vegetable sources, is absent here.

Hydrated carbonate of potash. For some purposes, especially for flint-glass making, potash entirely free from sulphate, but containing 12 to 18 p.c. of water, is manufactured as follows. Ordinary carbonate is dissolved to a strength of 142°Tw., or even above this; the solution is allowed to cool and settle, which causes nearly all the sulphate to separate. The clear liquor is evaporated in flat-bottomed pans to the state of a thick paste; the fire is now drawn out, and the mass is constantly stirred up till it has been converted into a coarse powder. It is less deliquescent than calcined potashes; its composition approaches the formula $K_2CO_3,2H_2O$.

Yields and costs.—With 5 cwt. batches the quantity used for making 100 kilos. of 95 p.c. potash is 150 to 154 kilos. sulphate 95 p.c. and and 160 to 200 kilos. limestone; with 3 cwt. batches only 145 to 149 kilos. sulphate and 130 to 160 limestone. The quantity of coal is 250 to 310 kilos., rather less with large than with small batches. Of 100 parts of coal 27 are used for mixing, 28 for firing the black-ash furnace, 19 for the first calcining, 15 for the second calcining, 11 for steam. The wages for 100 kilos. potash amount to 2·80 or 2·90 marks, the casks to 1 mark, repairs 3 marks, sundry expenses 3 marks.

Blügel (D. P. J. 233, 151) gives the following calculation for a well-managed works:—

(*a.*) *Manufacture of potassium sulphate.*

	Marks
100 kilos. chloride of potass., 95 to 98 p.c.	13·50
85 kilos. sulphur. acid, 142°Tw. (self made), at 4·50 . . .	3·83
25 coke, at 1·90	0·48
Wages	0·80
Repairs, depreciation, general expenses	0·80
	19·41
Deduct value of 110 kilos. hydrochloric acid 32°	0·55
Product: 117 kilos. sulphate . .	18·86
Hence cost of 100 kilos. ditto .	16·12

(*b.*) *Manufacture of potassium carbonate.*

	Marks
147 kilos. sulphate at 16·12	23·70
140 „ limestone at 0·80	1·12
275 „ coals at 1·30	3·58
Wages	2·80
Repairs	1·00
Interest and depreciation	1·00
General expenses	1·60
Casks	1·00
Commission on sales	1·00
Cost of 100 kilos. refined potash 95–98 p.c.	36·80

The quantity of potassium carbonate manufactured by the Leblanc process in Germany amounted to about 12,500 tons in 1879 and to about 20,000 tons per annum in 1883.

4. *Potash from felspar and other rocks.* The recovery of potash from rocks containing it in large quantities (sometimes up to 14 p.c. K_2O), which undoubtedly by their decomposition have furnished all the potash existing in the soil, and hence indirectly that obtained from vegetable and animal sources, has been attempted by a number of chemists for many years past without much success. The most promising process seemed to be that of Ward and Wynants, who ignited finely-ground felspar (orthoklas) with lime and fluorspar till the mass had fritted. On lixiviation potassium hydrate and silicate are dissolved by means of carbon dioxide. The silica is precipitated, and potassium carbonate can be obtained from the solution in a very pure form. Both this and all similar processes are quite out of the field, since the discovery of the Stassfurt deposits has opened out an incomparably more convenient source of potash, which is, at any rate, sufficient for hundreds of years to come. The proposal of Spiller (S. C. I. 1882, 128), heating felspar with calcium fluoride and sulphuric acid in order to obtain potassium and aluminium sulphate, has very little prospect of practical realisation.

5. *Potash from wood-ashes.* This was formerly the only source of carbonate of potash on a large scale. About the middle of this century it lost much of its importance through the rise of the vinasse industry; and, since the manufacture of potassium carbonate by Leblanc's process has more and more extended, that made from wood-ashes has correspondingly receded into the background. Nor is this result very much to be deplored, for the ready sale formerly obtained for potash from wood-ashes led to the devastation of forests at an alarming rate. On the other hand, it is a fact that in some localities the only use to be made of timber is its conversion into ashes, and extraction of potash therefrom; but the places where this can be called in any way a rational process are getting more and more scarce. Several of the brands formerly found in trade have become extinct now. Since the use of wood as fuel has also very much diminished during the last generation the collecting of ashes from this source, which were formerly sold to the potash manufacturers, is now too troublesome in most countries, and such wood-ashes are there only used for domestic and agricultural purposes. Only some parts of Russia, Transylvania, Illyria, Canada, and the United States, still furnish somewhat considerable quantities of commercial potash (pearl-ash, &c.).

Potash is an indispensable element for the growth of most plants, and is hence found in their ashes. But where it is associated with much silica and phosphoric acid the ashes contain but little carbonate, and are not available for the manufacture of potash. This, for instance, holds good of straw-ash. The only practically important source of potash is *wood-ash*; it is true that the ashes of several herbaceous plants contain a great deal more of potassium carbonate than the ordinary woods, and it has been actually proposed to grow such herbs for this manufacture, but this is irrational and without any hope of success, as these quickly growing plants exhaust the soil much more quickly than can be made up by the natural decomposition of the minerals composing it.

The following table shows the percentage of total ash and of potash in some of the more important woods and plants:—

	Ash per cent.	Potash per cent.
Pine wood	0·34	0·045
Poplar wood	—	0·075
Beech wood	0·58	0·145
Beech bark	—	0·153
Ash wood	1·22	0·074
Oak wood	1·35	0·153
Oak bark	—	0·420
Box wood	—	0·226
Willow wood	2·80	0·285
Elm wood	2·55	0·390
Vines	3·40	0·550
Thistles	—	0·500
Rush	—	0·508
Ferns	3·64	0·626
Nettles	—	2·503
Vetch	—	2·750
Wormwood	—	7·300

In Canada most potash is made from elm, birch, larch, and maple.

The potash is contained in these plants in the shape of sulphate, chloride, silicate, and organic salts. The latter, on calcining, are converted into carbonate, part of which may be hydrated if lime was present; any silica present will pass into potassium silicate, and this renders the manufacture of potash from straw quite irrational. Where soda is present in large quantities the potash obtained must also be of inferior value. Hence the quality of potash found in trade is very varying, quite apart from actual falsifications with coal-ashes, soda, &c.

The manufacture of commercial potash is a very crude process. The wood is burned in pits dug in the earth in places sheltered from wind. The collected ash (beech-wood ash is preferred to all other wood-ashes; vine stalks, ferns, &c., where obtainable in quantity, are still better) is spread on a stone floor, sprinkled with water, and worked through till it is evenly damp. Sometimes (in Canada) a little lime is mixed with it, which afterwards causes the formation of caustic potash. The damp ash is placed in casks provided with a false bottom, covered with straw, and water (preferably hot) is poured over it. After some time the liquor thus formed is drawn off by a plug-hole at the bottom; if it is about 32°Tw. strong it can be boiled down at once; the weaker liquors and washings are used for lixiviating fresh ash. The residue, which with this rough style of working still contains much potash, is a good manure.

The boiling-down is also generally a very rough process. In lieu of pans possessing a large heating-surface (pans fired from the top would be the best) usually circular cast-iron pots fired from below are employed, in which the liquor is boiled down to dryness. In spite of stirring up the mass before it becomes quite dry much of it burns fast to the pot, causing a great waste of fuel and a speedy destruction of the pot. In America the mass is heated nearly to redness, and is converted into greyish-pink compact 'pot-ashes,' which are assorted by official inspectors into 'firsts,' 'seconds,' 'thirds,' and 'unbrandables.' The brown crude pot-ashes are calcined in reverberatory furnaces, which causes the carbonaceous and other organic matter to burn away, the hydrate to be carbonated and the sulphide, &c., to be converted into sulphate. Too great a heat has to be avoided, because the mass would then fuse, and this would prevent the organic substance from being burned. The resulting product should be white or blueish—the latter from potassium manganate. A purer product is obtained by dissolving the product of calcination in water, separating the liquor from the insoluble substances, evaporating and calcining again; thus the American 'pearl-ashes' are made.

The common American 'pot-ashes' are frequently made with addition of so much lime that they contain the major portion of the potash in the caustic state; thus some of the silicate is also recovered which would be lost otherwise. This potash fuses below a red heat; it is therefore only boiled down till the mass solidifies on cooling and appears in grey, red, or black lumps. This description of potash must be even more carefully protected against attracting atmospheric moisture than ordinary commercial carbonate of potash, although this is also deliquescent. Such caustic potash is very much in request by soap makers; it takes less lime in making their ley, and causes less loss, just in proportion of the smaller amount of lime-mud.

'Purified carbonate of potash' is made from ordinary carbonate in two different ways. Either the carbonate is stirred up in an iron pot with 1$\frac{1}{2}$ or 2 times its weight of *cold* water, and the mixture which gets hot allowed to cool down before siphoning off the clear liquor. The sulphate and some chloride remains behind, together with the insoluble matter; the residue is not washed (which would cause the sulphate to be re-dissolved), but only pressed. The liquor, containing mostly carbonate, but also chloride and silicate, is brought to dryness, stirring it up to the end. Or else the solution is made with *hot* water, the residue is exhausted in the same way, the liquors are boiled down to sp.gr. 1·50 and allowed to cool, when the sulphate and some chloride crystallise out. This process is more expensive than the former. In order to make still purer carbonate for flint-glass, pearl-ashes are calcined with a little sawdust lixiviated, the clear liquor is boiled down and calcined, and this is repeated twice over; the last product is dried down till it is converted into granular 'crystallised' carbonate with 15 to 18 p.c. of water (*cf.* p. 284).

Analyses of commercial potashes, pearl-ashes, &c., from wood.

Origin	Quality	K_2CO_3	KOH	Total available alkali calc. as K_2CO_3	Available Potash calc. as K_2CO_3	Na_2CO_3	K_2SO_4	KCl	Analyst
American potash .	—	68	—	75·5	68	5·8	15·3	8·1	Pesier
" "	1	41·7	49·6	108·2	106·4	1·4	4·0	2·0	F. Mayer
	2	19·4	44·4	87·8	77·2	8·2	16·1	5·6	
" "	2	18·3	36·6	81·7	65·9	12·2	15·1	14·6	Grüneberg
	2	34·5	29·6	81·8	77·9	3·0	15·0	7·5	
Montreal potash	firsts	43·87– 26·16	50·03– 36·50	92·49– 89·82	88·83– 85·54	6·24– 2·84	16·07– 10·40	4·41– 1·68	Tatlock
	seconds	38·53– 21·71	42·44– 30·63	85·79– 85·08	76·24– 73·98	11·47– 8·52	18·92– 9·18	12·82– 6·13	
	thirds	46·31	6·14	72·10	53·86	17·81	20·53	7·63	
Canadian pearl-ashes	—	71·3	—	74.2	71·3	2·3	14·3	3·6	Pesier
" " .	—	65·0	—	70·2	65·0	4·0	21·0	7·0	Grüneberg
" "	1	77·50	—	80·98	77·50	2·86	11·65	2·65	Tatlock
	—	71·38	—	74·53	71·38	2·31	14·38	3·64	
Tuscan potashes .	—	74·1	—	78·0	74·1	3·0	13·4	0·9	Pesier
" " .	—	62·6	—	76·9	62·6	11·0	15·5	4·5	Grüneberg
Illyrian potashes .	1	89·3	—	89·3	89·3	0·0	1·2	9·5	
Hungarian " .	3	41·6	—	68·0	44·6	18·1	30·0	7·3	
Galician " .	—	46·9	—	51·6	46·9	3·6	29·9	11·1	
Russian " .	—	69·61	—	73·77	69·61	3·09	14·11	2·09	Pesier
" " .	—	50·84	—	66·78	50·84	12·14	17·44	5·80	Bastelaer

The potash from bamboo-cane, made in British Burmah (Romanis, C. N. 45, 158), testing 32·54 K_2O, 0·98 Na_2O, 18·72 KCl, 16·95 SiO_2, 8·07 CO_2, 2·71 SO_3, 1·10 Al_2O_3 and Fe_2O_3, 19·43 H_2O, partakes more of the nature of a silicate than that of a carbonate (like all other potashes made from graminaceous plants).

The quantity of wood potash produced in the whole world was estimated by H. Grüneberg, in 1873, at 20,000 tons per annum. Even then its production had very much receded in comparison with former times. The exportation from Russia, formerly the leading country in that respect, which in 1864 had been 11,000 tons, in 1873 had declined to 5,540 tons; New York, which in 1865 exported 2,610 tons, in 1873 only exported 388 tons. Of the American exportation, about one-tenth is pearl-ashes, nine-tenths caustic pot-ashes. At present the total quantity of wood potash annually produced cannot exceed 10,000, or at most 15,000, tons; great part of this is consumed in the countries where it is produced.

6. *Potash from beet-root vinasse.* In the last stage of the manufacture of sugar from beet-root a syrupy liquid is obtained, which, although containing a very large quantity of sugar, cannot be brought to crystallise, owing partly to the presence of organic impurities, but chiefly to the large quantity of salts present. The latter circumstance prevents the utilisation of such 'beet-root molasses' in a similar way to cane-sugar molasses. For a long time the only way of dealing with beet-root molasses was this: diluting them with water, neutralising their alkaline reaction with sulphuric acid, causing the liquor to enter into alcoholic fermentation by means of yeast, and distilling off the spirit (which is of rather inferior quality). The liquor remaining behind in the stills, called 'vinasse' in French or 'schlempe' in German, was formerly always led back upon the fields on which the sugar-beet had been grown. To some extent this is still done; nor can it be denied that this is, after all, the simplest and at the same time the most rational way of dealing with it, whereever it is practicable with respect of carriage, for in this way the mineral substances (especially potash and phosphoric acid) taken from the soil in the shape of beet-root crops, are given back to it in a soluble form, together with the nitrates formed in the plants, which are lost in every other process of utilising the vinasse.

On the other hand, the large quantity of potash contained in this liquor has, under ordinary circumstances, a greater commercial value, even deducting the expense of recovering it in the shape of carbonate of potash, than in that of liquid manure. This was pointed out about 1830 by Dubrunfaut, to whom is thus due the introduction of the very important industry of beet-root potash, which, however, took firm root only about 1850, first and always foremost in the north of France, then also in Belgium and Germany. In France this forms still the most usual way of dealing with molasses, whilst in Germany it has become more usual to extract the sugar by means of the osmose, the strontia, and the lime processes. The strontia process easily admits of recovering the potash in the shape of 'vinasse cinder'; but the dilute liquids, obtained by the osmose and the lime process, are usually only applied for manuring the fields. Pfeiffer (Kali Industrie, 101) estimates the potash contained in the beet-root-juice worked in Germany in 1883, calculated as 80 p.c. potassium chloride, at 15,000 tons, 8,000 tons of which was rendered back to the fields by the factories working the osmose and substitution processes, whilst 7,000 tons passed into molasses. Of the latter, about 1,350 tons were recovered in the shape of 'schlempekohle' from the strontia process, and 3,000 or 4,000 tons from the factories working the molasses for spirit. In France sometimes the osmose liquor is worked for potassium nitrate, which forms 50 p.c. of the 'salin' obtained by boiling down the liquor to 40° Baumé (D. P. J. 245, 192; 264, 510).

Sugar-beet may be said to yield about 1 p.c. of ash, nearly half of which consists of potash (calculated as K_2O), present in the juice to a great extent in the shape of nitrate and of salts of organic acids, all of which on calcining yield carbonate. Very little of it goes away with the sugar: nearly all remains in the molasses, which contain from 44 to 50 p.c. of sugar, 14 to 18 p.c. other organic substances, 16 to 18 p.c. salts, and 15 to 18 p.c. water; the ash amounts to 10 to 12 p.c. The ash is composed as follows, according to Krocker:

	Soluble	Insoluble
Potash	47·88	1·70
Soda	2·34	0·17
Lime	—	5·08
Sodium chloride . .	12·92	—
Sulphur bioxide . .	1·53	—
Carbon dioxide . .	22·39	4·00
Silica	0·85	0·22
Phosphorus pentoxide .	—	0·29
Lime, magnesia, ferric oxide (as phosphates)	—	0·63
	87·91	12·09

Heidenpriem found in molasses ash:

Potash	47·67	51·72 p.c.
Soda	8·00	11·43 „
Lime	3·12	5·04 „
Magnesia . . .	0·10	0·18 „
Carbon dioxide . .	27·94	28·90 „
$SO_3,P_2O_5,SiO_2,Cl,Fe_2O_3$.	6·16	9·33 „

Manufacture of vinasse-cinder (*salin, schlempekohle*).—The vinasse, a liquid of about sp.gr. 1·028, and always of acid reaction (purposely brought about for the sake of fermentation, comp. above), is neutralised with lime, and is then concentrated by evaporation. Since the profitable working of this process depends entirely upon the economical evaporation of a dilute liquid, much ingenuity has been expended in the evaporating apparatus. The heat must act both as top and bottom heat, the flame travelling between two pans, or over the top of a pan covered with an arch, upon which another pan is set so as to be indirectly heated. The most successful and most widely-employed system for this purpose is Porion's furnace, in which the evaporating-surface is largely increased by splashing about the liquid in the fire-gases by means of paddle-wheels revolving from 400 to 800 times per minute.

The heat required for evaporating the liquid is produced partly by an ordinary fire, partly by the combustion of the organic substance contained in the vinasse. When the latter has been brought to the syrupy state, say 60°Baumé, it is transferred from the iron pan on to the bed of a reverberatory furnace, immediately attached to it, on which it is altogether dried, whereupon it takes fire and itself produces a large amount of heat. This is aided by the nitrates contained in the mass. The heat must, however, be so regulated that the mass is not brought to fusion; when fused it would be difficult to lixiviate, and it would also contain lower oxidation-products of sulphur. The process is therefore finished when a carbonaceous mass has been formed, a sample of which yields with water on filtration a colourless solution. This is the 'salin brut' or 'schlempekohle' (=vinasse cinder), a product which was formerly largely sold in this state, and employed chiefly for soft-soap and for the manufacture of saltpetre from Chilian nitrate of soda; it is now generally worked up into carbonate of potash and other salts.

The composition of vinasse cinder varies between very wide limits, according to the soil on which the beet had been grown. Grüneberg (Amtlicher Bericht über die Wiener Ausstellung, 1, 399) gives the following figures as the average composition of this product:

Potassium carbonate .	30 to 35 p.c.
Sodium carbonate . .	18 to 20 ,,
Potassium chloride . .	18 to 22 ,,
Potassium sulphate . .	6 to 8 ,,
Insoluble (incl. carbon) .	28 to 15 ,,

but the analyses published by Sauerwein, Gohren, Kuhlmann, Esselens, Lefevre, and others, prove that the proportion of the ingredients may vary even more than that.

In lieu of burning the syrupy vinasse on the hearth of an open surface, C. Vincent (C. R. 84, 214) runs it, at a strength of 40°Baumé, into iron retorts, and carbonises it with condensation of the formed vapours, the recovered liquids being subjected to a special treatment. This extremely ingenious process, by which trimethylamine and methyl chloride were for the first time obtained as commercial products, together with methyl alcohol and ammonia, has been carried out on a large scale at Courrières, in the north of France, but has not extended beyond this. A modification of Vincent's process is that proposed by A. Zwillinger (Germ. Pat. 38,419), who carbonises vinasse, brought to the syrupy state, in a retort by means of superheated steam.

The following description is an outline of Vincent's process as far as it has been published. The cinder, obtained by heating the vinasse-residue in closed retorts, is very porous and easy to lixiviate; the potash made from it is very pure, and especially free from sulphate and sulphide. The gaseous products are submitted to a process of condensation quite similar to that usual at gasworks; a little tar and a considerable quantity of aqueous fluid is condensed, and a considerable quantity of permanent gases is left over, which may be used for heating purposes.

The aqueous liquid contains ammonium carbonate, sulphydrate and cyanide, methylic sulphide, methylic alcohol, trimethylamine, and the volatile monobasic fatty acids. It is neutralised with hydrochloric acid, and the major quantity of water is removed by distillation. The distillate contains, together with much water, methylic alcohol and methylic cyanide; by re-distilling it with lime, the methylic alcohol can be set free, and calcium acetate remains behind. From 100 kilos. of molasses $1\frac{1}{4}$ litres of methylic alcohol is obtained. The original liquid, concentrated by distillation and allowed to cool, yields a crop of ammonium chloride (about 2 kilos. for 100 kilos. of molasses). The mother-liquor (about 1·8 kilos.) contains principally trimethylamine hydrochlorate. It is further concentrated by evaporation, and the dry mass is subjected to prolonged heating. At 260° there begins a strong evolution of gases, and at 325° the decomposition is finished. The gases escaping consist of trimethylamine and methylic chloride, afterwards with much ammonia; they are passed through hydrochloric acid, which retains trimethylamine and ammonia, whilst methylic chloride passes on, is washed with water and collected in a gas-holder. The liquor is concentrated to a boiling-point of 140°C.; on cooling, nearly all the ammonium chloride crystallises out and trimethylamine hydrochlorate remains in the mother-liquor. The gaseous methylic chloride is dried, and by means of compression and cooling is condensed to a liquid, boiling at −23°C., which is sent out in strong wrought-iron or copper drums, and used principally in the manufacture of aniline dyes.

The theory of the decomposition of the dry trimethylamine hydrochlorate by heat is as follows. At first this salt is, like ammonium chloride, dissociated by heat, and much free trimethylamine is volatilised. The acid residue at a higher temperature undergoes the following reaction: $N(CH_3).3HCl = 3CH_3Cl + NH_3$. This explains the final decomposition into trimethylamine, methylic chloride, and ammonia.

Elsewhere the recovery of methylic chloride and trimethylamine does not appear to have been attempted, but in several places the ammonia has been recovered by various methods. Thus Baswitz (D. P. J. 245, 415) runs the vinasse, concentrated to 31 or 41°Bé., in a thin jet into red-hot retorts. The gaseous products pass through a pipe filled with pieces of firebrick and heated outside by waste heat; further on some tar is condensed, rich in pyrrol and pyridine bases, then the ammonia is absorbed in sulphuric acid; at last the methylic alcohol is condensed by cooling, and the uncondensable gases are returned to the fire. Each retort takes a charge of 360 litres of concentrated vinasse every 12 hours; the produce of 4 retorts is: 87·5 kilos. ammonium sulphate, 30 kilos. liquor containing amines, 4 to 4·5 kilos. methylic alcohol, 57·5 kilos. tar. (The process did not pay when the prices of the above products went down.) H. Hirzel (Z. 11, 346) employs a vacuum apparatus with mechanical stirrer. Borsche & Sohn (D. P. J. 244, 85) carbonise the vinasse with lime in order to increase the yield of ammonia; they assert that up to 80 p.c. of the nitrogen can be thus obtained as NH_3. Similar processes are those patented by E. Ernst (D. P. J. 244, 86; 245, 413), by Oppermann, by Gaillett, and by the Waghäusel Sugar Company (*ibid.*), Lederer and Gintl (*ibid.*) carbonise vinasse, or the liquors of the lime and osmose process in revolving drums by a continuous process, the gases being treated for the recovery of ammonia.

Other apparatus for treating vinasse are those of Kux (D. P. J. 247, 163), of Klauning (*ibid.* 261, 256), of Gontard (*ibid.* 258, 498), and of Theisen (*ibid.* 257, 405).

Working-up of the vinasse cinder.—The cinder is broken up into pieces of the size of a man's fist, or rather less, and is methodically lixiviated with hot water in the usual way. The liquor is run off at a strength of 23-32°Tw.

The black residue (grey after drying) contains from 8–12 p.c. of alkaline salts (partly being potassium sulphate, partly not soluble in water), 20–40 p.c. carbonaceous matter, containing a little nitrogen, 15–30 p.c. calcium carbonate, and a few p.c. of other earthy matters. The first evaporation takes place by means of steam coils, and is carried to 74–82°Tw., the concentration being higher in summer than in winter. Most of the potassium sulphate is now precipitated as a fine mud; after two hours' settling the clear liquor is allowed to cool down, when impure potassium chloride crystallises out. According to whether the salts are at once subjected to methodical washing or not, they contain less or more potassium carbonate, as shown by the analyses of Tissandier (W. J. 1868, p. 286). The analysis of a large number of French samples of such chloride (by Blattner, unpublished) yielded—

Potassium chloride .	66·21 to 87·55 p.c.
Potassium sulphate .	5·27 ,, 19·86 ,,
Potassium carbonate .	0·10 ,, 6·49 ,,
Sodium carbonate .	0·40 ,, 4·57 ,,
Water	1·40 ,, 8·79 ,,

This product is principally employed for conversion into sulphate, and further on into carbonate, by the Leblanc process.

The mother-liquor is further evaporated by open fire in wrought-iron pans with flat or saddle-shaped bottoms, in three stages, down to 127–142°Tw. During evaporation monohydrated sodium carbonate is separated, which must be fished out, and is purified by washing and calcining; on cooling down, up to 97°Tw., principally potassium chloride crystallises out, which is washed like that obtained previously, but beyond that strength the crystals consist principally of a potassio-sodium carbonate, $K_2CO_3,Na_2CO_3,12H_2O$, together with some hydrated potassium carbonate, $K_2CO_3,2H_2O$. The double carbonate is re-dissolved in a little hot water and evaporated down to 127°, during which operation nearly all the sodium carbonate falls out as monohydrated salt, and is removed by fishing. The mother-liquor from this operation is boiled down, together with the mother-liquor formerly obtained, and is, after proper settling, calcined in a reverberatory furnace. It yields a potash containing:

K_2CO_3	80–84 p.c.
Na_2CO_3	8–10 ,,
KCl	3–4 ,,
K_2SO_4	3–4 ,,
K_2SiO_3	0·25–0·5 ,,
K_2HPO_4	0·3–1·5 ,,
Insoluble	0·1–0·2 ,,

Part of the potassium sulphate is formed from sulphocyanide; and this salt itself is partly formed only during the evaporation from potassium ferrocyanide and sulphide, as witnessed by the ferrous sulphide, always precipitated together with the fished-out soda. This purification from iron is very important, and is sometimes promoted by purposely adding potassium sulphide to the liquors in sufficient quantity to precipitate the iron. Otherwise, even white potash is discoloured on contact with the air. Once calcined potash, when treated as above, is sufficiently pure and white, but otherwise it can be purified by re-dissolving, settling, and calcining. The following analyses show the composition of different descriptions of potash:—

Analyses of commercial vinasse potashes.

Origin	K_2CO_3	Na_2CO_3	K_2SO_4	KCl	Insol.	H_2O	Analyst
French potash . . .	53·9	23·1	2·9	19·6	—	—	Pesier
Valenciennes potash . .	79·0	14·3	3·9	2·8	—	—	Grüneberg
Refined potash . . .	92·68	3·98	0·43	2·45	0·06	0·50	Tatlock
,, ,, . . .	91·22	2·89	2·76	1·92	0·08	0·85	,,
,, ,, . . .	90·83	2·68	2·67	2·52	0·27	0·90	,,
,, ,, . . .	90·25	2·52	3·81	2·92	0·21	0·45	,,
Belgium crude ash . .	43·0	17·0	4·7	18·0	—	—	Grüneberg
,, ,, . .	34·3	13·0	11·0	23·5	—	—	,,
Magdeburg crude ash. .	32·9	18·5	14·0	16·0	—	—	,,
,, ,, . .	27·1	18·0	10·0	9·5	—	—	,,
Waghäusel (refined) . .	94·39	trace	0·28	2·41	0·18	—	v. Groningen
,, ,, . .	88·73	6·45	2·27	1·01	—	—	Keller
,, ,, . .	78·10	13·33	2·31	3·21	3·05	—	Tissandier
,, ,, . .	81·22	13·15	1·78	3·25	0·80	—	,,
,, ,, . .	91·25	4·73	0·80	2·61	0·61	—	,,

7. *Potash from suint.* The 'suint' or 'yolk,' which forms a third or more of the weight of raw sheeps' wool, was proved by Chevreul to contain, together with many other substances, a considerable quantity of potash, combined with fatty acids to a soluble soap. Maumené and Rogelet were the first, in 1859, to utilise this for recovering carbonate of potash from the wool used at and near Rheims and Roubaix, and their example has been followed elsewhere, but not to any great extent. 100 parts of raw wool are stated by Maumené to yield from 14 to 18 parts of salts, or about 5 parts of potassium carbonate; hence the 60,000 tons of wool annually imported into the United Kingdom ought alone to yield about 3,000 tons of potassium carbonate, none of which is recovered up to the present. Even at Roubaix, Rheims, and Elbeuf, in lieu of the 1,200 tons obtainable from the wool consumed there, only 150 tons per annum are actually recovered; the total production of suint potashes in France, Belgium, and Germany probably does not exceed

2,000 tons per annum. This is all the more to be regretted as the potash contained in suint in the ordinary course of washing raw wool in a running stream does not return to the soil, but merely contributes to the pollution of water-courses. But the difficulty in the way of generalising the recovery process is this, that it does not pay on the small scale, and that neither producers nor consumers of wool in the majority of cases will relegate the care of scouring their wool to a central manufactory, where it is doubtful whether the different parcels can be kept entirely distinct. It is thus preferred by most wool-growers to wash their own wool, and, if possible, to bring the washings again upon their meadows.

The process for working the wool for suint potash is as follows. Instead of washing the raw wool first in a running stream, and afterwards scouring it with soap, soda, or putrefied urine, the wool is, before the proper scouring process, submitted to a methodical lixiviation with cold water, either in a series of casks or tanks, or in mechanically-acting washers, for instance that constructed by H. Fischer (D. J. 218, 484 ; 229, 446). The dilute washings are always utilised for the first treatment of a fresh quantity of wool. Thus a brown liquor of about sp.gr. 1·12 is obtained, which is evaporated in iron pans of very different constructions where the fuel can be efficiently utilised—for instance, in the reverberatory furnace of Werotte, in which the flame is drawn through the liquid itself by means of an exhauster; or by means of discs fixed on a shaft revolving in the boiling-down pan. Thus a pasty mass is obtained, which is either calcined in an open furnace or submitted to destructive distillation in gas retorts, in order to recover ammonia and illuminating gas. The carbonaceous residue is lixiviated and the liquor is treated similarly to that obtained from vinasse cinder, producing, by fractional evaporation and crystallisation, successive crops of potassium sulphate and chloride. But as suint contains but little soda (in the case of inland-fed sheep only 2·3 Na_2O to 100 K_2O, with sheep fed on the sea coast 13 Na_2O to 100 K_2O), the crystallisation of the double carbonate of potassium and sodium does not take place, the liquor being directly brought to dryness and calcined.

Suint potash, if unadulterated, in fact contains but little soda, as can be seen from the following analyses :—

—	From Verviers					First quality		Second quality
	Tissandier			Werotte		Tatlock		
K_2CO_3 . . .	71·52	79·01	72·25	68·50	64·30	91·20	89·41	80·57
Na_2CO_3 . .	4·96	5·15	5·14	3·20	3·10	4·39	3·83	2·48
K_2SO_4 . . .	2·48	3·03	3·33	2·10	2·49	0·52	0·17	4·75
KCl . . .	5·88	6·12	7·04	12·50	16·88	1·97	1·67	4·51
K_2SiO_3 . . .	—	—	—	8·50	8·00	—	—	—
Insoluble . .	11·98	5·28	11·19	1·48	1·55	0·04	0·06	0·30
Water . . .	2·83	1·20	1·05	2·77	2·80	1·60	4·70	7·25

The following analyses, by W. Graff, give the composition of wool potash, made in Germany—viz. (*a*) by the simple steeping process, (*b*) and (*c*) by methodical lixiviation :—

	a	*b*	*c*
K_2CO_3 . .	31·16	75·01	71·40
K_2SiO_3 . .	17·44	0·62	1·50
K_2HPO_4 . .	0·50	0·71	
K_2SO_4 . .	2·00	4·12	5·32
KCl . . .	3·93	5·68	6·74
Na_2CO_3 . .	3·15	3·07	4·55
H_2O . . .	1·22	1·30	4·72
Insoluble . .	40·60	9·49	5·77

Potassium hydrate (*Caustic potash*). The majority of soap-makers prefer causticising their own carbonate of potash, as they mostly do not require to do this thoroughly. Still the manufacture of caustic potash in the solid state is carried on to some extent on the large scale, with black-ash made by the Leblanc process from potassium sulphate, precisely in the same manner as caustic soda is made, so that we can refer to that article. In this place we need only give the analyses (by Tatlock) of some samples of caustic potash made on the large scale :—

—	White	Brown or cream	
Potassium hydrate . .	77·64	75·64	74·05
Potassium carbonate .	4·62	2·54	3·14
Potassium sulphate . .	0·38	0·21	0·69
Potassium chloride . .	2·29	0·93	2·26
Potassium nitrite . .	0·87	—	—
Sodium hydrate . .	4·67	2·59	3·20
Soluble silica and alumina.	0·30	0·20	0·55
Insoluble matter . .	0·02	0·22	0·69
Water	8·84	17·80	15·80
Available potash, K_2O .	68·33	65·24	64·31
Available alkali, calculated as K_2O . .	73·83	68·28	68·08

Potassium silicate. Potassium silicate, or soluble potash glass, has approximately the formula $K_2O,4SiO_2$. It is prepared exactly like the more common soluble soda glass, by fluxing together white sand and carbonate of potash in a reverberatory furnace, preferably with a little charcoal, which aids in expelling the carbon dioxide by reducing it to monoxide. The following proportions are stated by N. Fuchs to be suitable : white quartz sand 45 parts, commercial potashes 30 parts, wood charcoal 3 parts, to be fused for five or six hours till no more gas escapes; the product is 58 parts of silicate. O. Schür prescribes: 90 sand, 62·5 potash, 1·5 charcoal; product 112·5 to 115 soluble glass. Some manufacturers employ sulphate in lieu of carbonate of potash, together with a larger proportion of charcoal, but this process is much more difficult than with carbonate. Solid potassium silicate is a transparent glass, tinged a bluish green, which is either sold as such, or in the state of a thick solution, produced by boiling it with water for a long time, preferably under pressure. Frequently (first by Fuchs) a mixed silicate of soda and potash is produced, either by using a mixture of potash and soda in the fluxing process, or by mixing the solutions.

Silicate of potash can be obtained also by dissolving very finely-divided silica (in the shape of ignited and ground flints, or of kieselguhr, or Farnham stone) in a very strong solution of caustic potash, by prolonged boiling, or in a shorter time by boiling under pressure. This process is actually used for the manufacture of silicate of soda.

The following analyses, by Tatlock, show the composition of commercial silicate of potash :—

—	Solid			Liquid	
	a	*b*	*c*	*d*	*e*
Potash (as silicate)	23·54	22·91	9·46	4·31	3·49
Soda (ditto)	1·28	1·28	1·52	4·20	1·80
Silica	65·60	66·84	23·28	24·32	16·64
Potassium sulphate . . .	0·87	1·08	0·67	0·61	1·48
Potassium chloride	0·48	0·48	0·41	0·67	3·52
Alumina and ferric oxide. . .	0·40	0·32	—	—	—
Water	7·83	7·09	64·66	65·89	73·07

The total quantity of potassium silicate manufactured is but small in comparison with that of sodium silicate; for mixing with soap it can be nearly always replaced by the cheaper sodium silicate. It is, however, used in fresco painting, and for a few other purposes.

Potassium nitrate (*Saltpetre, nitre*). Potassium nitrate KNO_3 is first mentioned by Geber, in the eighth century, and again by the alchemists of the thirteenth century. Agricola in 1546 gives a description of its manufacture from saltpetre earth, which does not materially differ from the present process. The artificial preparation of this substance from Chilian nitrate of soda is quite a recent process, due in the first instance to the greatly-increased demand produced by the Crimean war, but this manufacture has gained very large dimensions, and is now much more important than the working of natural saltpetre earths.

I. *Manufacture of saltpetre from natural saltpetre earths.*—Such earths are found principally in East India, where the district of Tirhût, in Bengal, is the most important one in this respect, and whence nearly all the natural saltpetre still manufactured is derived. Smaller deposits are found in Egypt, Persia, Hungary, Apulia, Kentucky, &c., none of which are of more than local importance now.

The raw material occurs only occasionally in real strata or nests; it is mostly a product, continually re-formed by the action of atmospheric air upon nitrogenous organic matter in the presence of bases, as lime, magnesia, and potash (for which, in Peru, near the sea-coast, soda is substituted). The organic nitrogen is not simply oxidised by atmospheric oxygen; the process of 'nitrification' never takes place except in the presence of certain microbes, as first proved by Schlösing and Müntz (C. R. 84, 602; 85, 1018; 86, 892), and confirmed by many subsequent observers (Warrington, Storer, P. F. and G. C. Frankland, Winogradsky, and others).

Whether the formation of ammonia is an indispensable intermediate link remains an open question. The nitrification process is, of course, much more intense in hot countries, where it is promoted by the abundance of organic matter, and by the moist and warm atmosphere. It is always dependent upon a supply of nitrogenous organic substances, and has nothing to do with the direct formation of nitric acid from atmospheric oxygen and nitrogen by the electric discharge. Saltpetre earth is, consequently, chiefly found in the neighbourhood of villages, where urine, &c., yields an abundant supply of organic nitrogen. In Bengal it is collected by a special caste, the 'Sorawallahs,' partly from the soil, partly from the surface of mud heaps, mud cottages, &c., by scraping off the uppermost layers which show a white efflorescence.

The following analyses show the composition of some Indian saltpetre earths :—

—	Tirhût (Stevenson)	Tirhût (J. Davy)	Ceylon (J. Davy)
Potassium nitrate .	0·7	8·3	2·4
Calcium nitrate . .	0·9	3·7	—
Magnesium nitrate .	—	—	0·7
Sodium sulphate .	2·7	—	—
Sodium choride . .	1·4	0·2	—
Calcium sulphate .	—	0·8	—
Magnesium sulphate	—	—	0·2
Calcium carbonate .	44·3	35·0	26·5
Insoluble in acids .	50·0	40·0	60·8
Water and organic substances . .	—	12·0	9·4

Ganges mud, according to Warneford Lock, contains 8·3 p.c. potassium nitrate, and 3·7 p.c. calcium nitrate. This earth is lixiviated in earthenware dishes, or wooden boxes, or in pits dug in the ground and made tight by a clay puddle. The liquor is concentrated in iron pots, or sometimes only by solar heat, and a crop of very crude saltpetre is thus obtained. The mother-liquor is further evaporated to obtain common salt, and the last mother-liquor, which contains a large quantity of calcium and magnesium nitrate, is mostly run to waste. Sometimes a somewhat more rational process is pursued, by mixing wood-ashes with the saltpetre earth previous to lixiviation, or adding such ash to the solution during concentration; the potassium carbonate of the wood-ash then converts the earthy nitrates into potassium nitrate. The crude saltpetre, obtained from the clarified liquor by slow evaporation in earthenware pots, is called 'dhouah;' it contains from 45 to 70 p.c. KNO_3, and is re-crystallised by native merchants, who sell it in this state as 'kalmee.' The following analyses, by Tatlock, show the composition of some samples of Indian saltpetre:—

—	Bengal ordinary 1	Commercial 2	Bombay 1	Crude 2
Potassium nitrate . . .	96·51	89·36	72·46	36·06
Potassium sulphate . .	0·89	0·75	0·13	2·64
Potassium chloride . .	0·84	4·57	6·65	—
Sodium nitrate . . .	—	—	—	0·26
Sodium chloride . . .	0·20	0·31	17·41	47·43
Calcium sulphate . . .	—	—	0·19	2·21
Magnesium nitrate . .	—	1·97	0·17	2·08
Insoluble	0·21	0·14	0·14	1·55
Water	1·35	2·90	2·85	7·95

A sample of the 'refuse salt,' left behind on recrystallising the first crop of crude saltpetre, contained 8·83 K_2SO_4, 13·15 KNO_3, 21·14 KCl.

The exportation of saltpetre from East India is about 25,000 tons per annum.

According to Ljubawin (Fischer's Jahresb. 1885, p. 262), there is a large deposit of saltpetre earth in the Khanat of Khiva, south-west of Fort Nukus, of the following composition:—

Soluble in water . . .	27·89 p.c.
Soluble in hydrochoric acid	17·14 „
Carbon dioxide . . .	5·73 „
Insoluble in acids . .	48·42 „
	99·18 „

The portion soluble in water contains:—

KNO_3 . .	5·52 p.c.	$CaSO_4$ . .	3·25 p.c.
$NaNO_3$ . .	4·05 „	$MgSO_4$ . .	0·66 „
$Mg(NO_3)_2$.	1·04 „	Total nitrates	10·61 „
NaCl . .	12·90 „		

Saltpetre earths are found, and are worked by processes quite similar to those used in India, in some places in Persia, Egypt, Spain, Hungary (near Debreczin) and elsewhere.

An *artificial saltpetre earth* is, or formerly was, prepared in some European countries (Hungary, Switzerland, Sweden) by mixing a porous soil containing much calcium carbonate, with decaying animal substances; for instance, by preparing such a soil underneath the floor of stables where cattle and sheep are kept, whose urine penetrates into the soil, and there undergoes the nitrification process. In Sweden, where formerly every landowner was obliged to furnish to Government a certain quantity of home-made saltpetre, all sorts of animal refuse was used up in this manner, in special 'saltpetre plantations.' About 100 tons per annum were made in Sweden in this way, but this process has been given up as unprofitable. In France, during the wars of the Revolution, when Indian saltpetre was inaccessible, that process was made compulsory by a decree of the Convention, and it is asserted that 2,000 tons per annum were then made in this way; but there also the home manufacture had to be given up as soon as saltpetre could be imported from the East. Since the manufacture of saltpetre from nitrate of soda is making a severe competition even to Indian saltpetre, it seems quite hopeless to look for that substance to European sources; here the nitrogenous substances are better utilised for agricultural purposes.

Another kind of crude saltpetre, made from the mother-liquors of the working of 'caliche' for nitrate of soda, is sometimes sent to Europe from South America. It contains from 16 to 26 p.c. of potassium nitrate, 51 to 77 p.c. of sodium nitrate, 1 to 3 (exceptionally 16) p.c. of sodium chloride, and small quantities of sulphates and iodates. Its value is hardly greater than that of its equivalent of ordinary commercial nitrate of soda.

According to Sacc (C. R. vol. 99, p. 84), in Bolivia, near the village of Arané, East of Cochabamba, a large deposit has been found of the following average composition: 60·7 potassium nitrate, 30·7 borax, traces of common salt, and water, 8·6 organic matter. If this were confirmed, it would be very valuable indeed.

Refining of saltpetre.—The East Indian saltpetre, before it can be used for the manufacture of gunpowder and other purposes, must be purified, especially from chlorides. This is done on a very large scale in England, France, and Germany (especially at Hamburg). The most usual is the French method. In an iron or copper pan 1,050 kilos. saltpetre is dissolved in 600 litres of water at a gentle heat; the solution is brought to boiling heat, and another 1,800 kilos. of saltpetre is dissolved in it. When employing these proportions with saltpetre containing about 20 p.c. of chlorides, the nitrate is dissolved completely, the chlorides but partially. The latter are fished out with a perforated ladle. If calcium or magnesium salts are present, potassium carbonate is added till a fairly alkaline reaction has been produced. The hot clear liquor is diluted with 300 litres of water, a solution of 1 kilo. glue in 20 litres of hot water is stirred into it, and the whole brought to boiling again. The glue combines with the organic substances present to a kind of scum, which rises to the surface and is carefully removed. When no more scum rises to the surface, the liquor is allowed to settle for twenty-four hours, preventing any cooling down below 90°C., and the clear portion is run into flat copper coolers. As soon as the crystallisation begins, the liquid is constantly stirred, either by hand or better by machinery. Thus the potassium nitrate separates as minute, floury, crystals, which do not, like large crystals, inclose mother-liquor in hollow spaces. The crystal flour is drained; the mother-liquor (500 to 600 kilos.) is used over again in dissolving fresh saltpetre.

The small crystals must now be washed to remove all adhering mother-liquor. This is done in vessels provided with a perforated false bottom, covered with linen. When all liquor has drained off, the bottom tap is closed, cold water is sprinkled upon the salt by means of a rose, the whole is allowed to stand for some hours, and only then the liquor is run off. This is repeated several times, until the liquor shows next to no reaction upon chloride. The last liquors are used in a new operation for the first washings. In this way the chlorides may be brought down to 0·005 p.c.

The drained crystal flour is dried in stoves or frames covered with canvas, or better on steam-heated pans, with mechanical stirring (just as they have been described for potassium chloride, p. 274), and is mostly sold in this shape. Sometimes it is required in the shape of large crystals, which are very easily obtained by dissolving the flour in a small quantity of hot water and allowing the liquor to cool quietly and slowly. Exceptionally, it is fused into cakes or drops, which always contain a little nitrite (the 'sal prunellæ' or 'nitrum tabulatum' of pharmaceutical chemists).

II. *Manufacture of potassium nitrate from nitrate of soda.*—'Artificial saltpetre' was first made on a small scale by Longchamps and Anthon, with the aid of Chilian nitrate of soda and of potassium chloride, which, however, at that time was only obtainable from kelp, and was too expensive. When, in consequence of the increased demand for saltpetre during the Crimean war, especially in Russia, the manufacture of that substance from Chilian nitrate of soda became more remunerative, it was first carried out, in 1853, by Nöllner, Grüneberg, and others, with the aid of caustic potash and of Russian carbonate of potash; later on, more cheaply, with that of *vinasse cinder* ('schlempekohle,' *cf.* p. 287), which was used directly, without any separation of the salts. For this purpose nitrate of soda and a corresponding quantity of vinasse cinder were dissolved at the same time in boiling water; by the reaction $K_2CO_3 + 2NaNO_3 = 2KNO_3 + Na_2CO_3$ anhydrous sodium carbonate was produced, which was fished out of the boiling liquid, together with the sodium carbonate originally present, and with the less soluble potassium salts, while the potassium nitrate remained dissolved at boiling heat and only crystallised out on cooling. The mother-liquor yields a mixture of about 53 parts NaCl, 31 Na_2CO_3, and 10 K_2SO_4, which is used by soap-makers (*cf.* D. P. J. 118, 200; 155, 418; 163, 314; 166, 75; C. C. 1872, 491). This process has been given up long ago, principally because the separation of the salts is too difficult and the value of potassium carbonate is too great.

The separation of the substances is easier when *caustic potash* is employed, in which case the reaction produces potassium nitrate and caustic soda; the mixture can then be allowed to cool. The potassium nitrate is all but completely separated as fine crystals, and sodium hydrate, with some impurities, remains in solution. By further concentrating this, solid caustic soda can be obtained. This process was carried out by Nöllner, Landmann, and Schnitzer (D. P. J. 117, 68; 162, 132) in this way, that to the boiling mixture of potassium carbonate and sodium nitrate lime was added till the alkali was causticised, whereupon the liquid was separated from the lime-mud, concentrated by evaporation, and allowed to crystallise. Much more rational than this was the process carried out at St. Helen's in 1864 (D. P. J. 182, 385), decomposing potassium chloride by sulphuric acid, converting the potassium sulphate by Leblanc's process into a kind of black-ash, dissolving and causticising the caustic solution to sp.gr. 1·50, adding an equivalent quantity of nitrate of soda, and allowing the potassium nitrate to crystallise by cooling. The mother-liquor was further concentrated, during which operation some salts were separated and fished out, and on cooling yielded a second crop of potassium nitrate; the second mother-liquor was worked up as caustic soda. This process does not seem to be worked now.

The process of Bolley (W. J. 1860, 201; 1866, 227), converting nitrate of soda by means of barium chloride into barium nitrate, and converting this by potassium sulphate into barium sulphate ('permanent white') and potassium sulphate, is evidently not fit for general use, and can only pay in very exceptional circumstances.

The only process now in practical use is that of employing *potassium chloride*, originally proposed by Longchamps, and worked out by Anthon (since 1840, but more especially in 1858, D. P. J. 149, 39), in the shape in which it is now carried out. It has been described in detail by Lunge (*ibid.* 182, 385) and Pick (*ibid.* 215, 222), and is carried out in several modifications, the best of which will now be described.

Stassfurt 'muriate of potash,' with not below 80 p.c. KCl, and commercial nitrate of soda (95 p.c.), are brought together with mother-liquors from a previous operation and with the liquid obtained by washing the nitre bags. The operation is performed in covered wrought-iron cylinders, 8 feet diameter and 6½ feet high, provided with a mechanical stirrer, a steam coil, and a tap for an open jet of steam; also with a 6-inch pipe in the cover, through which the steam given off in the cylinder is passed under the double bottom of the mother-liquor tank. The liquor is first concentrated by means of the steam coil to sp.gr. 1·53, adding a little oil in case of frothing, whereupon the materials are charged through the man-hole, first 3 or 3½ tons of nitrate of soda, then the corresponding quantity of potassium chloride, which is so calculated that a very slight excess of nitrate is present. The whole is boiled for half-an-hour to complete the decomposition, and is then run through a

4-inch tap on to the filter or strainer, consisting of a tank 8 by 8 by 5 feet, with a canvas-covered false bottom at a height of 4 inches above the true bottom, and a steam-pipe between the two for keeping the liquor hot. Here the sodium chloride formed in the reaction $NaNO_3 + KCl = KNO_3 + NaCl$, which, owing to its relatively slight solubility in the hot concentrated solution, had been almost entirely precipitated in the solid form, is retained on the filter, while a liquor of sp.gr. 1·63 and a temperature of 95°C. runs off into the coolers. The common salt left on the filter is covered with hot mother-liquor, which is run off at a strength of 1·50 to 1·53, also into the coolers. The washing is then continued with liquors of decreasing strength, ultimately with pure water, till the salt contains only 0·6 to 0·9 p.c. of nitrate; at some works they go down to 0·25 p.c. The coolers are shallow iron vessels provided with either oscillating or revolving agitators, which can be lifted out of the liquid. The liquor is kept in agitation during the whole time of cooling, which, with a depth of 8 inches in the vessels, ought to be finished in thirty to thirty-six hours. Sometimes this is hastened by a stream of water circulating on the outside of the vessel.

The mother-liquor, of sp.gr. 1·345–1·357, is run off into tanks provided with a double bottom, where it is heated by waste steam in order to be used over again at the first operation. Such mother-liquors are composed as follows. 100 parts by volume contain:

	a	*b*	*c*
Potassium nitrate .	29·40	25·5	26·4
Sodium chloride .	25·72	14·2	17·18
Sodium sulphate .	1·32	1·06	1·81
Magnesium chloride	2·10	6·2	8·19
Sodium nitrate .	—	19·6	7·19
Sodium iodide .	—	—	0·76

(*a*, sp.gr. 1·348 at 19°C.; *b*, sp.gr. 1·395 at 17·5°C.; *c*, remaining after working up 5,000 tons of Chilian nitre).

The crude saltpetre flour, containing 7–9 p.c. NaCl, and 0·5–0·7 p.c. $MgCl_2$, is drained on one side of the cooler, and is washed with the liquor resulting from the washing of the refined saltpetre, with the use of the agitating gear, till the chloride has come down to 0·8–2 p.c. It is then refined by dissolving it in washings of the pure salt to sp.gr. 1·53–1·55, filtering as above, and running it into iron coolers; in doing this, a very small quantity of ultramarine is added, to neutralise the discolouration produced by a small quantity of iron. Here a mother-liquor of the following composition is produced:

	a	*b*
Potassium nitrate . .	20·91	23·4
Sodium nitrate . . .	1·02	—
Sodium chloride . .	5·94	4·4
Sodium sulphate . .	0·12	—
Magnesium chloride . .	0·78	1·1

(*a*, sp.gr. 1·184 at 17°C.; *b*, sp.gr. 1·180 at 18·5°).

The crystals produced at the same time still contain 0·25 to 0·75 p.c. NaCl, and must be purified by washing them with water in copper-lined iron vessels, in the manner described above for potassium chloride (p. 273); this produces a liquor of sp.gr. 1·075–1·083. The washed salt is drained, and is dried upon shallow, circular cast-iron pans, heated by means of steam channels in their interior; a revolving shaft moves the salt about by means of scrapers forced down by springs, and a conical roller at the same time crushes any lumps formed in drying (*cf. Potassium chloride*, p. 274). Each such pan dries nearly 4 tons of nitrate in twenty-four hours. Unavoidably, some crusts are formed at the bottom, which must be knocked off once a day. The dried saltpetre need only be passed through a sieve to be ready for packing into casks.

It is asserted that, when German muriate of potash is employed, traces of magnesium chloride may remain in the saltpetre and render it deliquescent; this is to be counteracted by adding as much soda-ash as will throw down the magnesia. Muriate of potash made from kelp contains no magnesium chloride, but from 6 to 8 p.c. of sulphate, which does not decompose with nitrate as easily as the chloride. In Germany the above-mentioned drawback has never been found; nor can it be conceived that a mode of manufacture which actually brings down the total chloride to 0·01 p.c. should leave anything whatever of the extremely soluble magnesium chloride in the saltpetre.

The 'saltpetre salt'—that is, the impure sodium chloride formed in this manufacture—contains about 98 p.c. of NaCl in the dry state, with 0·25 to 0·9 KNO_3 and slight quantities of other matters. The nitrate makes it unfit for decomposing with sulphuric acid on account of the strong action on the iron pans; it is used for agricultural purposes, and for roasting the cinders from cupreous pyrites in the process of copper-extracting by the wet method.

In the United Kingdom annually about 32,000 tons of pure nitrate of potash are manufactured, partly from about 12,000 tons of imported Indian saltpetre, the remainder by means of nitrate of soda. About 30,000 tons are used in the manufacture of gunpowder and other explosives; the remainder is used for pyrotechnics, for lucifer matches, for curing meat, as a flux in metallurgical assays, for some descriptions of fire-extinguishers, in medicine, &c. Very large quantities of nitrate of potash are also made in that way in Germany, Austria, France, &c.

Potassium arsenate KH_2AsO_4 (Macquer's salt) is manufactured by fusing together equal parts of potassium nitrate and white arsenic (arsenious anhydride), dissolving the mass in water, and evaporating; on cooling the liquor the arsenate crystallises out in large, soluble, quadrate crystals, which do not deliquesce in the air. This salt is used in calico-printing as a substitute for cow-dung.

Potassium bichromate. This salt, commercially known as 'bichrome' or 'bichromate of potash,' is, strictly speaking, potassium pyrochromate, its formula being $K_2Cr_2O_7$. It is the commercial product from which all other chrome compounds used in the arts are manufactured, and it is itself always made from *chrome iron ore*, all other natural occurrences of chrome being comparatively insignificant.

Chrome iron ore is altogether analogous to magnetic iron ore, the ferric oxide being replaced by chromic oxide. Its typical formula is therefore Cr_2FeO_4; but the Cr_2O_3 is always partially replaced by ferric oxide and alumina, the FeO by magnesia. Manganese protoxide and silica are also frequently present. Hence the proportion of chromic oxide present in the ore varies between 30 and 65 p.c., that of ferrous oxide between 20 and 36 p.c. The following analyses by Clark show the composition of different samples of chrome ore as shipped to the consumers:

—	*a*	*b*	*c*	*d*	*e*
	p.c.	p.c.	p.c.	p.c.	p.c.
Cr_2O_3 .	57·00	52·60	46·02	40·40	34·40
Al_2O_3 .	14·00	13·19	14·90	25·09	19·09
FeO . .	12·00	14·14	16·07	14·14	14·14
CaO . .	0·67	trace	trace	0·67	0·67
MgO . .	15·00	14·72	15·85	13·83	20·90
SiO_2 . .	1·60	4·80	7·25	6·00	10·80
H_2O . .	—	0·70	0·20	—	0·30

Clouet (D. P. J. 193, 33, 40) gives the following as the average composition of the ore from various localities:—

—	Cr_2O_3	FeO	Other constituents
Ile-à-Vaches (crystals) .	51·54	48·6	—
Baltimore (lumps) .	45·00	42·31	12·69
Wilmington (smalls) .	45·50	42·78	11·72
Christiania (smalls) .	40·00	37·77	22·23
Var, in France (lumps) .	37·00	34·79	28·21
Hungary (lumps) . .	31·48	29·60	38·92
Jekaterinenburg, Ural .	49·49	23·27	27·24
Orenburg, Ural . .	53·00	24·92	22·08
Karahissar, Asia Minor .	53·00	24·02	22·08
Trondhjem, Norway .	42·00	19·72	38·28
Styria	53·00	24·92	22·08
Wjatka, Russia . .	58·00	18·18	23·82
Orsowa, Banate . .	48·72	18·33	32·95
India	47·50	35·70	16·80
California . . .	42·20	23·84	33·96
Shetland Islands . .	42·60	23·50	33·36
Australia . . .	33·20	23·40	43·40

The manufacture of bichromate of potash from chrome iron ore is always founded on the fact that chrome oxide, even in combination with FeO, &c., when ignited with an alkali in a current of air, forms a chromate of the alkali present, from which the more easily crystallisable bichromate is afterwards obtained. Formerly the oxidation of Cr_2O_3 to CrO_3 was promoted by employing potassium nitrate, but this process has been given up long ago, because atmospheric oxygen, under proper conditions, suffices for the object. It is, however, not advisable to simply heat the chrome ore with potassium carbonate, because the reaction takes place above the fusing-point of potassium carbonate, and the fusion impedes the action of oxygen upon the bulk of the mixture. Stromeyer first proposed the addition of lime to the potassium carbonate, which prevents the mass from fusing and keeps it in a porous state, so that the oxidation can proceed right through. Jacquelain went so far as to replace the potash entirely by lime, but his process does not seem to be practicable on a large scale. Tilghman, Swindells, and other inventors have tried to replace the carbonate of potash by chloride, &c., but their processes have not answered.

The following account of the manufacture of bichromate of potash, as carried on in Great Britain, was communicated to Dr. Hoffmann by Mr. Rowland Atcherly (Bericht über die Wiener Ausstellung von 1873, i. p. 725):—

'The chrome ore, preferably Turkish or Asiatic, which contains but little ferric oxide and silica with a comparatively large quantity of chromic oxide, is first crushed by stamps, then ground in horizontal mills and passed through a sieve with 80 holes to the superficial inch. The fine powder is carefully mixed, in cylinders revolving round a diagonal axle, with potash-lime, prepared on the spot from burned Irish limestone and a solution of potassium carbonate in the proportion of 7 cwt. of lime to 2 cwt. 1 qr. of K_2CO_3. Care must be taken that the potassium carbonate employed is free from chloride, as this would interfere with the subsequent crystallisation of the bichromate. The limestone should contain but little combined silica, and no sodium or magnesium. This potash-lime, which, when properly prepared, has a thoroughly dry appearance, is mixed with $4\frac{1}{2}$ cwt. of the ground and sifted ore in the above-described manner. This mixture forms the weight of a charge for the roasting which now follows. The furnace employed has a level hearth, 9 feet long and 6 feet wide. The distance between the roof and the furnace-bed is 2 feet 6 inches, and is gradually contracted to 18 inches on passing into the outlet flues. The flame is blown down upon the hearth by means of jets of steam. The furnace-bed is provided with two fire-clay doors, through which the charge is introduced, and is spread in a layer of about 2 inches depth over that half of the bed which is nearest the fire. The operation is begun with heating up the furnace. The draught should not be too strong, and the fire should not crackle; but care must be taken that the mixture is exposed to an oxidising flame. The temperature of roasting is a bright-red heat. Every quarter of an hour the mass is turned over with a plough-like instrument, and thus a new surface is exposed to the action of the flame. After two hours the man gradually moves the mass on to the other half of the furnace-bed, and into the space now vacant a new charge is introduced. The mass is still turned over every quarter of an hour. A properly-conducted roasting operation should be finished in four hours. The proportion of chromic oxide converted into chromic acid should not be less than 90 per cent. of the total amount present in the ore. The properly-roasted material has a greenish-yellow colour; it is interspersed with hard lumps, possessing a bright-yellow fracture, and consists of potassium and calcium chromates, with free lime, potassium silicate, and ferric oxide. It is, when cool, crushed to a coarse powder, and is charged into wooden lixiviating vats.

'The mass is here treated with a hot solution of potassium sulphate, which converts the calcium chromate previously formed into calcium sulphate. The lixiviating vats are so disposed that the solution of potassium sulphate, after having passed down one of the vats, flows on to the surface of the next following one, so that ultimately a saturated solution of potassium chromate is obtained. The calcium sulphate, still suspended in that solution, is allowed to settle down in deep vessels. The clear liquid is now conveyed into the decomposing vats, which are lined with lead. A sufficient quantity of concentrated sulphuric acid, diluted with twice its volume of water, is added to it and the mixture is allowed to cool. Since a solution of chromate, saturated at 16°, contains nearly one part of salt to two of water, whilst bichromate requires ten parts of water for its solution, it follows that on converting a saturated solution of chromate into bichromate, and cooling, about three-fourths of the bichromate must be precipitated. The precipitate is collected and recrystallised; the mother-liquor, which contains potassium sulphate, is employed for the treatment of the roasted mass as above. The bichromate crystallises best in deep iron vessels from a solution of sp.gr. 1·120. Within the liquor strings are suspended, and the temperature is kept at about 21°.'

It is evident that the roasting of the mixture of chrome ore or potash-lime would be much better carried out in a revolving or other mechanical furnace, where the continuous renewal of surface, and their constant exposure to the oxidising flame, would be much more thoroughly effected than in ordinary hand-wrought furnaces.

The following modifications of the ordinary process have hardly come into practical use on a large scale.

J. Booth (patent of 1853) first ignites the chrome ore, finely mixed with coal, till the iron has been reduced to the metallic state; this is extracted by sulphuric acid and recovered as copperas, whilst the remaining porous chromic oxide is treated in the usual manner.

F. O. Ward (patent of 1864) adds to the usual mixture some fluorspar, which is to cause the reaction to take place more quickly and at a lower temperature.

Tilghman recommended treating the chrome ore with a mixture of potassium sulphate and lime. According to H. Schwarz (D. P. J. 198, 157), the potassium sulphate does not take any part in the roasting process, but facilitates the lixiviation. Drummond and Donald (Eng. Pat. 2,594, 1877) mix 100 parts of chrome ore with 250 lime, 125 potassium sulphate (or 100 sodium sulphate), and 40 sulphuric acid, and roast the mixture as usual. Their idea is that the alkaline bisulphate is to decompose the chrome ore, but how can bisulphate be formed in the presence of lime?

J. Pontius (Germ. Pat. 21,589) commences the operation as usual, by roasting chrome ore with potash and lime. The mass is lixiviated with mother-liquor from previous operations, containing a sufficient quantity of potassium carbonate to convert all the calcium chromate into potassium chromate. The liquor is now treated in closed iron vessels with carbonic acid under a pressure of several atmospheres, whereby potassium bichromate and bicarbonate are formed:

$$2K_2CrO_4 + 2CO_2 + H_2O = K_2Cr_2O_7 + 2KHCO_3.$$

The bichromate, which is but slightly soluble, is precipitated and is separated from the mother-liquor, which serves for treating a fresh quantity of roasted mass. Or else the latter is treated at once with carbonic acid and hot water under pressure, in closed iron vessels provided with mechanical agitators. Hereby the neutral potassium chromate is converted into bichromate and bicarbonate; the calcium chromate is also converted into calcium bichromate, which at once reacts with potassium carbonate and forms potassium bichromate.

Formerly the manufacture of bichromate of potash was principally confined to the United Kingdom (especially Glasgow); the production of other countries was not very large. Recently it has been very much extended, both in the United Kingdom and abroad, chiefly in consequence of the great demand for the manufacture of alizarine and other artificial colouring matters, but chromate and bichromate of soda are now taking the place of potassium bichromate in many cases. In 1868 the total production of bichromate was estimated at about 3,000 tons per annum; ten years later the United Kingdom alone produced about 10,000 tons per annum, and several thousands of tons are manufactured in Germany, Russia, North America, &c.

Potassium (and recently sodium) bichromate is very extensively employed, both for the preparation of compounds containing chromium and for its oxidising properties. A large series of colours, which are salts of chromic acid, is made from it; but there is also a series of colours ('lakes') consisting of chromic oxide combined with organic colouring matters, and both of these facts cause a very extended application of bichrome in dyeing cotton and wool, in tissue-printing, and in the manufacture of chrome colours, serving as pigments. As an oxidising agent, bichrome has a most varied application for the manufacture of coal-tar colours (principally alizarine), for the bleaching of oils, &c. In certain photographic processes it is indispensable, gelatine mixed with potassium bichromate becoming insoluble by the action of light. This property has been also utilised for preparing insoluble glue. G. L.

POTATO OIL *v.* FUSEL OIL.

POTATO STARCH *v.* STARCH.

POTTER'S CLAY *v.* CLAY.

POTTERY AND PORCELAIN. The term 'pottery' is a very elastic one, being commonly used to indicate any article fashioned of clay (or of a mixture of clays and other earthy substances) and hardened by the application of fire. Used in this sense the term includes, besides all kinds of crockeryware, such common articles as flooring and roofing tiles, drain-pipes, bricks, and fireclay crucibles. Nor is there any adequate reason why this comprehensiveness should be curtailed, for though a vase of Sèvres china and a common drain-pipe are widely different when finished, they come equally well within the scope of our definition, and their production depends on the application of exactly similar principles, the superior result attained in the one case being mainly the result of superior elaboration and care.

Potteryware of every kind is usually divided into two great classes.

1. Simple or unglazed, such as flooring and roofing tiles, bricks, terra-cotta, &c.

2. Composite or glazed, such as the ordinary forms of porcelain, tableware, &c.

This distinction is largely an arbitrary one, for almost every kind of ware is capable not only of existing in both forms, but of serving some useful purpose in each of them. The terms are, however, not without value, in so far as they help us toward an easier conception of the terms 'body' or 'paste,' and 'enamel' or 'glaze'; a ceramic paste being the stuff or substance of which the article is first fashioned or shaped, and the glaze or enamel a coating on this, resulting from the application of vitrifiable substances to the body, either to render it impervious to liquids, or to serve æsthetically as a means of decoration. A clear conception, then, of the various ceramic pastes, of the processes by which they are produced, and of their relationships to each other, forms the safest starting-point from which to review the science of the potter.

The foundation of every pottery paste, without exception, is one or other of the various natural clays, for the bare possibility of a pot, as we know it, results from the two properties which the clays alone, among natural substances, possess in any marked degree—viz., the property of being kneadable while moist into almost any required shape (what we term plasticity), and secondly the property of becoming dense, hard, and durable when fired. While, however, the possession of these properties renders the use of some natural clay unavoidable, many other qualities are required of a good paste which can only be secured by the addition of other materials, natural or artificial. Thus, articles made from a plastic clay alone are apt to crack in drying, owing to the tenacity with which such clay retains its included water; in firing they are apt to soften a little, especially if the clay contains much iron or lime, and so lose their shape; these defects necessitate the admixture of sand, ground flint, or other aplastic or hardening material, so as to make the body opener or less retentive of water, or to render it less liable to soften in the firing from partial fusion. Again, in some classes of potteryware, translucence is a necessary quality of the fired paste, and this can only be secured by due admixture of the clay with certain fusible materials which, when submitted to the heat of the pottery oven, vitrify, and enveloping the minute particles of clay with which they are associated produce a semi-transparent substance.

All the substances which are in general use in the composition of ceramic pastes may be divided into three classes according to their function—

1. Plastic materials: all the varieties of clay and marl;

2. Hardening or aplastic materials (Fr., *dégraissantes*): flint, sand, quartz, ground pitchers, &c.;

3. Fusible materials: felspar, china stone, bone ash, lime, gypsum, barytes, artificial fritts, &c.;

and the object of the potter is to select from the materials at his disposal such of them as will enable him to produce a body that will suit his conditions of firing and working. Thus it happens that in nearly every country of Europe in which pottery is manufactured on the large scale, one form has become to a certain extent national, and the expressions French porcelain, German stoneware, English earthenware, show how local conditions have to a certain extent prescribed the manufacture.

The current classification of pottery into earthenware, stoneware, porcelain, &c., is thoroughly unscientific, for the distinctions on which it is based, such as colour, hardness, and translucency, are mainly accidental, and may be due quite as much to the methods of manufacture and the degree of heat at which the ware is fired as to any inherent difference in the pastes themselves. It is impossible in the present state of our knowledge to draw any hard and fast line between the different kinds of pottery; but, perhaps the following classification, designed to bring out the natural relationships of the pastes, has as much to recommend it as any:—

First class.—Pastes containing only plastic materials, or a mixture of plastic and hardening materials. It is impossible to separate this into two classes, as the question whether any hardening material must be added depends entirely on the nature of the particular clay in question. In this class the following forms would be included: bricks, tiles, common stoneware, and the common red and brown ware of all countries. The fired body is always opaque, moderately hard, and generally strongly coloured red, grey, or buff.

Second class.—Pastes containing plastic, hardening, and fusible materials. The pastes of this class naturally present a wide range of qualities, varying according to the proportions in which the three classes of materials enter into their composition. The fired bodies are hard, dense, generally opaque, and white or pale in colour. All the better kinds of English earthenware, stoneware, granite, and mortar bodies are included in this class.

Third class.—Pastes containing plastic and fusible materials only. All the finer kinds of pottery—such as hard-paste porcelain, soft-paste porcelain (both natural and artificial), parian, jasper, &c.—belong to this class. The fired bodies are very hard, durable, and translucent, and, unless stained by the addition of colouring oxides, are white or creamy in colour.

Preparation of the paste.—In the preparation of all pastes for the potter's use the first object to be aimed at is perfect homogeneity, and the more complex the paste the more important does attention to this point become. For pastes of the first class it is usually sufficient to remove stones and other hard foreign matter, and then to pass the clay through a pug-mill or a mortar-mill to insure its being sufficiently well mixed; but for bodies belonging to the second and third classes, where high finish and mechanical perfection of shape and surface are required, it is essential that all the materials be reduced to a very fine state of subdivision in order to bring about the intimate admixture of the various constituents that is desirable. The processes for this purpose are much the same with all kinds of pastes, and it will only be necessary to describe the methods used in preparing the paste for English earthenware (in many respects the most elaborate and complicated of pastes), as the processes used in its preparation are quite suitable, with slight modifications in detail, for the preparation of all the other pastes.

The substances used for this particular paste, are: ball clay from Devon or Dorset, china clay from Devon or Cornwall, china stone from Cornwall, and boulder flints from the sea beaches of Newhaven, &c. The clays used vary greatly in plasticity, and the proportions of ground flint and stone with which they are mixed will depend largely on this quality of the clay. The proportions used for a good average cream-colour paste are: ball clay 50 p.c., china clay 10 p.c., flint 37 p.c., stone 3 p.c. The clays are beaten up to a pulp with water, in a blunger or iron chest in which a shaft carrying broad-bladed knives is rapidly rotated. This liquid paste is known technically as 'slip.' The flint and stone require to be reduced to an impalpable powder, in order that their particles may be uniformly diffused among the particles of clay in the slip. The flints are first calcined, usually in specially-constructed kilns; this calcination having rendered them white and friable, the nodules are then broken into coarse lumps in an ordinary stone-crushing machine, and finally charged on to a pan similar to the one shown in section in fig. 1.

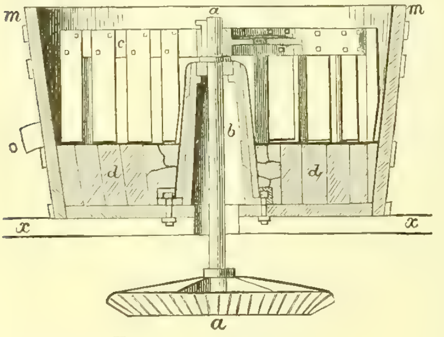


Fig. 1.—Grinding-pan.

x. Floor line. *m*. Pan sides. *d*. Pavement of chert. *a*. Driving shaft, working in centre tub *b*, and carrying arms *c* which drive large blocks of chert over the face of the pavement *d*.

The pan is built up from the floor, either with iron sides, or with wooden staves strongly hooped together. The bed or bottom (*d*, fig. 1) is a pavement of chert stones, and from 8 to 16 inches thick, according to the size of the pan. Over the face of this pavement large blocks of chert, weighing sometimes as much as half a ton each in the case of large pans, are driven round and round by the arms (*c*) fixed on the vertical shaft (*a*). The fragments of calcined flint, or of other material to be ground, are charged on to this pavement (*d*), a little water is run in, and a grinding of longer or shorter duration, according to the weight of the grinding stones, suffices to reduce the materials to fine powder in suspension in water. This form of pan is in general use for the grinding of all pottery materials, such as flint, stone, felspar, glaze, &c., that are required in the state of powder. The material of the pavement and of the runners is, of course, ground away, and hence it is advisable to have them of some substance whose introduction into the paste, in small quantities, will not cause any serious disturbance of its properties. The paving-stones are obtained from the Halkyn Hills in Flintshire, from Bakewell in Derbyshire, or sometimes blocks of granite from Skye are used. The runners are obtained from the chert in the mountain limestone near Bakewell, and it is essential that they should be as free as possible from bands of carbonate of lime. A pan of this description, 12 feet in diameter, and carrying a load of from 5 to 6 tons of chert runners, should grind 1 ton of flints in 12 hours.

Having thus obtained all the materials in a state of fine subdivision, and in suspension in water, each material is run into a separate vat, the cubic contents of which are known. The sp.gr. of each of the slop liquids being ascertained, the requisite proportions of each are run altogether into a big vat or blending ark, and thoroughly mixed together by means of agitators. This method of slop-blending—at best a rough volumetric one—though in most general use, is far from being reliable, owing to the difficulty of accurately gauging the contents of the large arks in use, and the difficulty of making the correct allowance for any slight variations in the densities of the slop materials used. For the finest bodies it is now customary to weigh out accurately the requisite proportions of dry, finely-ground material, and then to agitate the whole mixing together with water, taking care to wash out all the mixing vessels afterwards.

When the materials have been mixed in this way they are carefully sifted through fine brass and silk sieves to remove all coarse particles, dirt, &c., and then finally magneted to remove any particles of metallic iron or of magnetisable iron compounds which may have come in by way of the ball clay or from the machinery used, and which, if left in the paste, produce after firing black specks of Fe_3O_4, a quite unsightly disfigurement in white bodies. In this country the magneting is performed by running the slip through a box or spout containing a number of horseshoe magnets suspended in it so as to almost touch the bottom; a much better apparatus is to be found figured and described on pp. 515–16 of the volume on 'Porcelain' forming tome v. of Fremy's Encyclopédie Chimique. The whole slip mixture, having been thus cleansed, is in condition to be made into clay for the potter. Two methods of doing this are in widespread use. The older method is one of evaporation, by which the prepared slip is run on to shallow brickwork kilns to a depth of from 6 to 8 inches, and then slowly dried to the consistency of potter's clay by fires burnt under the kilns. This process is now in use only where small quantities are to be operated upon, or where many different pastes are made in small quantities; and the clay produced in this way needs very careful beating together to render it of one consistency throughout, while it is liable to contain hard lumps of clay that have been burnt from contact with the brickwork; the process, too, is slow, and therefore quite inadequate for the production of such large quantities of clay as are required in the great potworks of this and other countries. The method now adopted in all works where large quantities of clay are required is one of filtration under pressure. The slip is delivered, by force pumps working up to a pressure of about 76 lbs. on the square inch, into strong canvas bags supported between fluted wooden trays strongly clamped together. The bags expand a little until they fill the space between each pair of trays, and then, acting as a filter, the water is driven through the pores of the cloth and a mass of plastic clay is left behind. The time taken up in this operation depends on the nature of the paste; pastes like those for porcelain, granite-ware, &c., which contain only a small proportion of plastic material, part with their contained water readily; but plastic pastes like those used for the best varieties of earthenware, and containing much ball-clay, retain their water more obstinately, and take a longer time to attain the right consistency. The clay or paste, as it is delivered from the bags, is always harder on the outside of the cake than on the inside, and is then either thoroughly beaten together or is put through a pug-mill to render it uniform in consistency and free from air bubbles.

Some reference must be made here to the very obscure phenomena connected with what is known as the 'ageing' of ceramic pastes. It is an old and well-known fact that all ceramic pastes improve in plasticity, firmness, and working qualities generally, if they are kept for a considerable time after making, and are occasionally watered, beaten, and turned over. These changes have been attributed to a fermentation taking place in the clay; but the word 'fermentation' appears to have been very loosely applied here. In most cases there is an undoubted evolution of gas, generally of CO_2 and H_2S; but this is clearly accounted for by the slow oxidation, in presence of air and moisture, of vegetable remains (fine rootlets, &c.) and of the iron pyrites, which are almost invariably contained in the natural plastic clays. In all probability the change is mainly a physical one brought about by the gradual settling of the mass, owing to the slow evaporation of water and the consequent shrinkage of the whole. That the change is largely of this nature seems to be borne out by the fact that paste made from scraps and broken fragments of unfired clay vessels is always more plastic than newly-made clay; in fact, at Sèvres and other places where pastes are used possessing but little plasticity it is customary to throw a lump of the clay into a round mass on the potter's wheel, dry it somewhat, then shave it down into thin shavings in the lathe, and re-make these into clay again. By repeating this series of operations—a process which can, of course, only be used for the manufacture of the most expensive articles—it is found that the paste becomes considerably more plastic and workable than when freshly prepared.

The paste being ready, then, for the hands of the potter, some consideration must be bestowed on the method of fabricating the desired articles from it, and these methods vary both with the shape and size of the article, and with the nature of the clay. With round articles and with a very plastic paste, the oldest of all pottery processes—that of 'throwing on the wheel'—is adopted; but with articles of oval or irregular shapes, or with pastes possessing but little plasticity, other methods have to be adopted, and of these the most important are pressing and casting.

Pressing is a term used to indicate two quite distinct processes—first, plastic pressing, in which the article is made from clay; and, secondly, dry pressing, in which the article is stamped out of clay previously dried and reduced to fine powder. In plastic pressing the clay is beaten out into a thin cake or bat, which is then pressed by the workman into moulds of plaster of Paris, baked clay, sulphur, or metal, which are generally made in sections so as to be readily taken to pieces. When each portion of the mould has had a bat of clay applied to it and rubbed down into all its lines and indentations, the portions are fitted together, tightly strapped up, and then the seams or joints are all rubbed down so that the clay forms one piece inside the mould. On standing, the clay dries a little; in drying it contracts slightly, and thus releases itself from the mould; when the clay is sufficiently hard to bear handling, the mould is taken to pieces, the clay article taken out, its seams and edges trimmed down and sponged smooth, and the article is put to dry in a hot-air stove preparatory to firing. The enormous quantities of tiles now used in the internal decoration of buildings are prepared by the dry-pressing process. The paste, after a careful preparation as detailed above, is taken from the filter press, dried white dry in a steam-shed, and then ground to powder in a disintegrator or between rollers. This dust is slightly damped, so that if a handful of it be squeezed it adheres loosely together. The damped dust is then put into a metal mould, a die is pressed strongly down upon it by means of a screw, and the tile is thus literally stamped out of dust. A tile thus made is possessed of sufficient adhesion to bear the handling necessary to fire it, and when fired it becomes hard and sonorous, though probably not so hard or so durable as a tile made from clay by the old plastic process.

Casting—the third method in general use for the fabrication of pottery articles—is the simplest of all methods, and is mostly used for those compositions which do not produce a very plastic paste, such as those required for the ordinary porcelain and parian bodies. The mixed slip is not made into paste or clay at all; but, after being got to such a density that a pint of the liquid mixture weighs about 30 oz., it is poured into moulds made of plaster of Paris. The plaster being porous, absorbs water from the slip, and a thin coating of clay is thus formed on the inside of the mould. When this coating is of sufficient thickness, the still liquid portion of the slip is poured out, and the mould and its clay-cast are set to drain. After all superfluous liquid has drained away, it is placed in a hot-air stove; the clay-cast shrinks away from the mould, and can then be drawn out or the sections of the mould taken away from it, smoothed off, thoroughly dried, and it is then ready for the operation of firing.

Though applied with slight differences of detail to suit different pastes, and with the introduction of much machinery for the saving of labour, these three methods of throwing, pressing, and casting comprise in principle all the methods used in the fabrication of pottery. Details of most of the processes in use, especially in

French factories, with drawings of plant, appliances, &c., will be found in Brongniart's Traité des Arts Céramiques, and in vol. 5 of Fremy's Encyclopédie Chimique. There is no practical English work on the subject.

The following table exhibits in percentages the composition of the most important pastes in general use: —

Sèvres porcelain (*pâte dure*): kaolin 48, felspathic sand 48, chalk 4.
Berlin porcelain (*pâte dure*): kaolin 75, felspar 25.
Meissen porcelain (*pâte dure*): kaolin 73, felspar 25, ground porcelain pitchers 2.
Vienna porcelain (*pâte dure*): kaolin 72, felspar 12, quartz 12, gypsum 4.
English bone china (*pâte tendre naturelle*): kaolin 27, china stone 27, bone ash 46.
English cream-colour earthenware: ball clay 50, china clay 10, flint 35, stone 5.
English white earthenware: ball clay 25, china clay 32, flint 34, stone 8, oxide of cobalt ·05.
English white tile body: ball clay 28, china clay 28, flint 40, stone 4.
English granite ware: ball clay 25, china clay 25, flint 40, stone 10, oxide of cobalt ·08.
English terra-cotta: red marl 90, flint 5, Cornish stone 5.
English parian: china clay 36, felspar 64.
English mortar body: ball clay 25, china clay 20, stone 55.
English evaporating pan clay: ball clay 25, china clay 14, stone 46, flint 15.
English fine white stoneware: ball clay 25, china clay 20, flint 10, stone 45, oxide of cobalt ·02.
English black clay: red marl 75, oxide of manganese (MnO_2) 6, calcined clay ironstone 19.
French siliceous faïence: china clay 24, chalk 24, flint or sand 48, fritt 4.
Fritt for above: sand 85, K_2CO_3 7, $NaHCO_3$ 3, $CaCO_3$ 5.
French tile body: ball clay 25, chalk 25, sand 15, crushed firebrick 35.

The percentages given above represent pastes of good quality and in actual use; but almost every potter in this country has his own mixing, arrived at in almost all cases by rule-of-thumb method, and good only so long as there is no change in the quality of the materials or in the processes. No attempt has ever been made to arrive at the theoretically best composition for any given paste, except in the case of hard porcelain, where the succession of distinguished chemists in the laboratory at Sèvres—Brongniart, Malaguti, Salvetat, Ebelmann, &c.—have brought their manufacture to a high pitch of perfection, but without making the business a commercial success.

Firing of the paste.—The firing of the ware is one of the most important branches of the potter's business, for the durability and economic value of any kind of pottery largely depends on the way in which it has been fired. Each paste requires a different method of firing, or a different degree of heat, to yield the best results. It may be safely stated, as a general rule, that bodies of the first class do not require so much heat as those of the second class, nor those of the second so high a temperature as those of the third class. A good clear red heat is quite sufficient, for instance, for the burning of ordinary bricks; the bodies of the second class, known as earthenware and stoneware, require a clear white heat (60°–70° of Wedgwood's pyrometer); while of the bodies of the third class, English bone china requires about 85°–110° Wedgwood, and hard paste or true porcelain requires the highest point attainable in pottery ovens, a blue-white heat, corresponding to about 150° Wedgwood, or a little above the melting-point of grey cast iron.

Bricks, tiles, drainpipes, and other coarse pottery are exposed directly to the flames, and may, indeed, be burnt in heaps or clamps, though the burning in ovens or kilns is now largely superseding the old wasteful method of burning in the open. For the finer bodies, however, such as those of the second and third class given above, direct contact with the fire, except when the articles are to receive a salt glaze, is inadmissible, and such articles are therefore always inclosed or carefully packed in fire-clay boxes known as saggers (Fr., *cazettes*), and these are piled one upon another, each pile of saggers being called a 'bung,' in a large chamber built of firebrick, into which the flames play, and which, indeed, forms a kind of vertical, cylindrical, reverberatory furnace. The form of furnace used, the methods of firing, and the sequence of operations are so different in the case of hard paste porcelain from that pursued with the other bodies that they demand a separate notice quite apart from the general subject of firing.

Hard-paste porcelain is, without doubt, the highest form of pottery, but, owing to the lack of a sufficiently refractory fire clay and to various other causes, its manufacture has never attained a permanent foothold in this country. In various countries of the Continent it is, however, largely manufactured, and in the table given above will be found the composition of the pastes used at the various imperial factories. From the composition of these pastes it will readily be perceived that they can possess but little plasticity, and the manufacture of large and difficult articles is a most laborious and costly process. But the most distinctive feature of this form of pottery is the thinness of its glaze, and the perfect accordance that exists between the body and the glaze, so that they dilate and contract equally under variations of temperature, and agree so well in composition that the glaze is never subject to *crazing*, the incurable fault of so much glazed ware of other classes. This perfect agreement is due not only to the complete agreement in composition between the body and the glaze, but also to the method in which they are fired together, so that the glaze actually interpenetrates the body to an appreciable depth, and becomes, as it were, one substance with it.

When the articles have been made and dried sufficiently they are first of all submitted to a very low heat in a globe or chamber (B, fig. 2) placed over the oven proper, and heated by the waste heat from it. By this operation, known as '*feu dégourdi*,' the articles are thoroughly dried, and rendered just hard enough to take a coat of glaze without breaking. The glaze consists simply of felspar, similar to that entering into the composition of the paste, or of a mixture of felspar and quartz (*v.* under *Glazes*) ground to fine powder and held in suspension in water. The article, after the *dégourdi* stage, is dipped in this, or the glaze is pencilled on it, and, on drying, a coating of fine glaze powder is left on the article. The articles are then carefully placed in saggers made of the most refractory fireclay, and elaborate precautions are taken to support them, so that they shall not touch each other or the sides of the saggers in which they are placed; they are also propped and supported from certain points so as to diminish the risk of their going out of shape in the firing, owing to the partial fusion of the body and glaze which takes place. The saggers, with the ware, are then placed in the oven A (fig. 2) in piles or bungs until the oven is conveniently filled. The doorway D is bricked up, and a fire is started in each of the mouths C, of which there are from four to eight or ten at equal distances round the oven. In many cases two or more of such chambers, with mouths, &c., are built above each other, and the waste heat from the first one is conducted through the others in such a way that when the first oven is fired up the one above it is about half fired, and so a much smaller quantity of fuel is needed in order to finish it off. The form shown in fig. 2 is, however, the most modern form in use in Limoges, the great seat of the French pottery industry. The fuel used in most places is wood, because it gives a longer, clearer flame than coal. In many of the Continental potteries, however, coal is now coming more largely into use, though the fumes from the pyrites &c. contained in it, the volatile alkaline vapours given off from some coal in burning, and the fine particles of ferruginous ash carried over from it, are all liable to bring about defects in the porcelain if they penetrate into the saggers through any cracks caused during firing. (For the comparative value of the different fuels *v.* art. FUEL.) The firing is allowed to go very slowly for about 12 or 20 hours, so as to expel the moisture gradually and raise the temperature slowly to a red heat, beyond which all danger of cracking from sudden and unequal expansion ceases. The fires are then gradually increased, and are maintained for a period varying from 60 to 120 hours, according to the size of the oven and the fuel used. When fired sufficiently, the mouths are closed and the oven is allowed to cool very slowly.

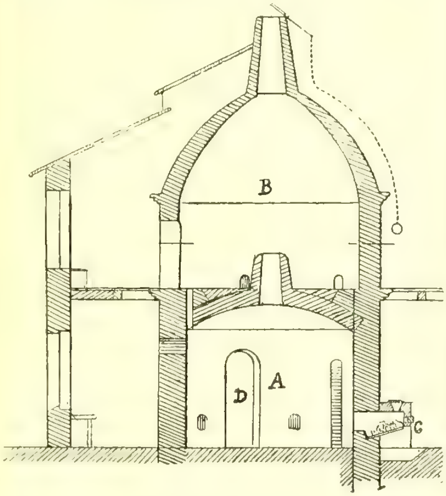
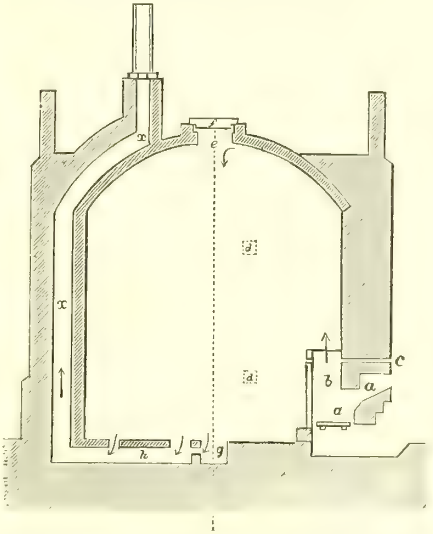


FIG. 2.—OVEN FOR HARD-PASTE PORCELAIN.

A. Oven proper. B. Globe where the ware is hardened before glazing. C. Mouth or fireplace. D. Door.

Other bodies.—With all other glazed bodies—except those which are so vitrifiable as to need no glaze, becoming of themselves impervious to liquids, and those which are to be salt-glazed (*q.v.*)—there are two distinct firings of the ware. In the first, known as the biscuit firing, the clay article is heated up very strongly, becoming hard, compact, and sonorous, and, though generally porous, it is yet rendered sufficiently durable to be applicable to many useful purposes. To render it impervious to liquids, or to serve various decorative purposes, the ware thus burnt, and known as 'biscuit' or 'bisque,' is dipped in glaze and then re-fired at a temperature sufficiently high to completely vitrify the glaze upon it. This second fire is known as the 'glost' fire, and is always of less intensity than the 'biscuit' fire.



Across one of the chimneys. Across one of the mouths.

FIG. 3.—VERTICAL SECTION OF MINTON'S PATENT OVEN.

a. Mouth. *b.* Bag or short chimney into oven. *c.* Peep-hole. *d.* Holes for drawing trials. *e.* Crown-hole, closed during firing by damper *f*. *g.* Well-hole, communicating with flues *h*, which open into chimneys *x* in the walls of oven.

The ovens used for the biscuit-firing are shown in figs. 3 and 4.

The form of oven shown in fig. 3 above, and known as the down-draught oven, is a modern improvement on the older form fig. 4. Here there are no flues running from the mouths under the floor of the oven, but all the flame plays into the oven by the short upright bags *b*. The flames go up the side of the oven to the roof or crown; but, as the damper *f* is kept closed during the firing, the flame is reverberated down through the central portions of the oven, and the smoke and fumes are drawn out of the oven through the well-hole g and the flues h, which open into chimneys x inclosed in the wall of the oven in the space between each pair of mouths. As the heat is more confined and more evenly distributed in this form of oven than in the old form shown in fig. 4 and described below, there is a larger yield of well-fired ware from it, and the same quantity of ware is fired with a smaller consumption of coal. This form of oven is, however, more costly to build, and unless the proportion of air space in both mouths, chimneys, and oven is carefully regulated, one portion of the oven may be heated sufficiently while another part may be relatively cold. The ovens used in this country range in size from 12 to 18 feet in internal diameter, and an oven of the latter size will hold about 2,000 saggers, each containing from one to a score of pieces. An oven of this size consumes about 10 to 12 tons of coal in a firing of from 60 to 80 hours. The points to be mainly attended to are, firing very slowly at the commencement so as to expel any water remaining in the pieces very gently, or the ware is apt to be violently ruptured, then gradually raising the heat and keeping it regular and equal in all parts of the oven, and at no time either suddenly increasing or checking it.

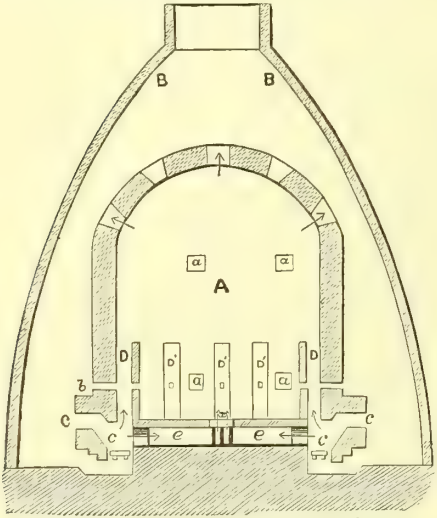


Fig. 4.—Common or Up-draught Oven.

A. Body of oven. B. Hovel or hood. C. Mouths. D. Bag or upright chimney. D′. Other bags. *b*. Peep-hole. *e*. Bottom flues under floor of oven, running to well-hole x. *a*. Trial holes.

Fig. 4 represents the old or up-draught form of oven, in which the flame from the mouths C C, of which there are from eight to ten arranged at equal intervals round the oven, plays directly into the body of the oven A by the short upright chimneys or bags D D′ &c. Besides these chimneys, flues E E run from each mouth to a well-hole x in the centre of the oven floor; over this well-hole a bung of perforated saggers, known as the pipe bung, is run up to the top of the oven or crown, and a portion of the flame is thus drawn into the centre of the oven. The ware is bedded in sand or ground flint in the saggers, which are then piled in the oven from floor to ceiling, with spaces left between the piles of saggers or bungs to admit the free play of the flame among them. Holes are left at intervals all round the crown to permit the escape of the fumes and smoke. The hovel or hood B is built over the whole oven, to protect it from high winds and to create a good draught. The piles of saggers being arranged in rings round the central pipe bung, and the mass of flame playing up the walls of the oven, it follows that the ware in the centre of the oven always receives less heat than that in the saggers nearer the oven walls; it is therefore necessary to arrange the position of the pieces in the oven in such a way that the thick heavy pieces shall get the most fire, and the flat or thin pieces least, as they are most liable to become distorted if over-fired.

Various attempts have been made to improve the methods of firing, or the style of oven in use, but the only other oven that seems likely to meet the requirements of the bodies produced in this country is one patented recently by A. J. Wilkinson of Burslem (*v*. Eng. pat. 4,356, March 20, 1890). This form of oven is a combination of the two forms described above, for while there are flues from each mouth to a central well-hole as in the older form of oven shown in fig. 4, the flame, products of combustion, &c., instead of passing directly out of the oven as in that form, are drawn out by horizontal flues running from the well-hole, between the firing flues, and opening into vertical chimneys in the walls of the oven between each pair of bags, as in the 'Minton' oven shown in fig. 3. Whether this form of oven will be a practical and economic success remains to be seen.

The question of gas-firing has also received a good deal of attention, especially in America, France, and Germany. Ovens and kilns are said to be at work in Trenton, N.J., and East Liverpool, Ohio, fired with natural gas. In France, M. Dubreuil, of Limoges, claims to have successfully overcome the difficulties of firing hard porcelain with producer gases; while, in Germany, Messrs. Siemens and Hoffmann have been equally successful at Berlin. Gas-fired regenerative kilns are in use in this country for firing bricks (*v*. Eng. pat. 3,862 of 1881, and Eng. pat. 17,573, 1890), but little progress has been made in applying the process to firing pottery.

Effects produced on a paste by firing.—We must now consider the changes produced in a paste by the action of firing. The most obvious effects are changes in colour, hardness, and density, an entire loss of plasticity, often an increased porosity, and always a shrinkage in bulk, or contraction.

Loss of water.—The first effect of firing is the expulsion of all the water left in the paste. The paste before firing contains water in two conditions—first, the mechanically-held water that has been used to render the paste sufficiently plastic for use; second, the water of combination of the argillaceous constituents of the paste (*v*. art. Clay). The *contained* water is readily expelled at a temperature of about 110°C., but the water of *combination* is not expelled in all cases by prolonged exposure to a temperature of 300°C., and in the case of very plastic pastes a full red heat is required to entirely expel the combined water. Expulsion of the contained water alone causes merely a slight shrinkage of the paste, and consequently a slight alteration in its density, the plasticity remaining undestroyed up to that point; but when once the point has been reached at which the water of combination is expelled the paste becomes hard and sonorous, loses all its plasticity, and will no more combine with water however finely it may be ground.

Hardness.—One of the most notable qualities of natural clays is their property of becoming hard and durable when raised to a red heat; but in the case of ceramic pastes, containing other materials besides plastic ones, the degree of hardness acquired is often different from that of a natural clay heated to the same temperature. The more fusible matter a paste contains the greater is its hardness at all temperatures above that at which fusion begins, while bodies containing a large excess of free silica, or an excess of lime, can generally be scratched by a good knife, even after a severe fire. As a general rule, the hardness of the fired body agrees with its density, while it almost invariably increases with an increased temperature of firing. The following rough classification shows how the different pottery bodies stand in this respect:

1. Scratched with a knife, readily. Almost all ancient pottery and majolica (body).
2. Scratched with a knife, but with difficulty. Bodies of the first class, of modern manufacture.
3. Not touched by a knife, but abraded by a good file. Well-fired earthenware (biscuit).
4. Not scratchable by a steel tool. Bodies of the third class, and some stoneware, and mortar bodies.

Density.—The variations in density which pottery pastes undergo in firing are by no means well understood. With ordinary bodies there is generally an increase in density, varying with the degree of fire; but with some of the bodies of the third class the increase in density appears to be very irregular. Thus with English bone porcelain, and, according to Brongniart, in the case of hard-paste porcelain too, although there is a considerable shrinkage of the paste in firing, yet not only does the body lose weight in firing, but it loses it at such a rate as to outstrip the loss of size, and thus the density of the fired body is less than that of the unfired paste. English bone china, again, when over-fired, suddenly suffers a great diminution in density, attended by an expansion of the article.

Shrinkage.—The contraction which all pastes undergo in firing depends on two things, (*a*) the nature of the paste, (*b*) the method of fabrication of the article. Contraction due to the nature of the paste either results from the expulsion of the water contained in the paste, and this may cause a contraction of from 10 to 15 p.c. in pastes with a very large proportion of plastic constituents, or it may result from the partial vitrification of the fusible constituents of the paste; thus Parian body (*q. v.*) which contains a large proportion of felspar, runs in as much as 20 p.c. from the dry size in being fired up to translucence. The influence of different proportions of plastic, aplastic, and fusible materials in the paste is well shown by the case of the three following bodies:—

No. 1.

Ball clay	10 p.c.
China stone	7 p.c.
Flint	80 p.c.
Lime	3 p.c.

No. 2.

Ball clay	25 p.c.
China clay	10 p.c.
China stone	60 p.c.
Flint	5 p.c.

No. 3.

Ball clay	60 p.c.
China clay	20 p.c.
China stone	10 p.c.
Flint	10 p.c.

The three bodies were fired to the same temperature (80°Wedg.), being placed in the same sagger, in the form of dry tiles pressed from dust. No. 1 exhibited no contraction, No. 2 ran in 25 p.c., and No. 3 ran in 20 p.c.

The contraction due to the loss of water is merely a physical change, but that due to the vitrification of the fusible materials may be in part a chemical one, due to the formation of new compounds. The effect of the two processes is strongly marked in the case of hard porcelain, which when submitted to the first or hardening fire (*feu dégourdi*) shrinks about 3 p.c., and this from loss of water, which is entirely expelled by this firing; but when this dehydrated ware is raised to incandescence a further contraction, amounting to nearly 7 p.c., takes place, and this is mainly due to the fusion of some of the constituents of the paste.

The method by which any given article has been fabricated also modifies the amount of contraction; the ware subjected to the greatest pressure in making will contract the least in firing, with any given paste. Thus, moulded or pressed ware runs in less than thrown ware, and this considerably less than cast ware, though all may be made from the same paste and fired to the same temperature. Thrown ware always has a tendency to form ridges or inequalities of the surface, due to varying pressure of the hands of the thrower in working up the ball of clay; thrown ware also exhibits a constant tendency to untwist, so to speak, in the firing, and indeed there is little doubt that every thrown piece when fired does go back a little from the shape into which it has been set by the manipulation of the thrower.

Colour.—For the effect of fire on the colour of ordinary ferruginous clays *v.* art. Clay, and see also Appendix A, p. 276, of Catalogue of Pottery in Jermyn Street Museum. As almost all natural varieties of plastic clay contain traces of iron sufficient in amount to produce at least a pale cream- or ivory-coloured body when fired, it is customary in the production of very white earthenware to add a small quantity of CoO, which by the production of a feebly-blue silicate of cobalt neutralises the effect of the yellow tone due to the iron compounds; 1 part of CoO is sufficient to whiten about 2,000 parts of cream-colour paste. Excess of flint and china clay and addition of lime or magnesia to the paste also whiten the fired body to a marked degree (*v.* also art. Clay).

For specially coloured pastes see further in section on colours in this article. The following table gives the percentage composition of some of the more important pottery bodies after firing:—

—	Silica	Alumina	Lime	Magnesia	Potash	Ox. of Iron	Bone Earth	Analyst
Sèvres hard paste porcelain, 1770–1830	58·00	34·50	4·50	—	3·00	—	—	Malaguti
Vienna (Imperial) hard paste porcelain, 1806	61·50	31·60	1·80	1·40	2·20	0·80	—	Laurent
Berlin hard paste porcelain, 1808	66·60	28·00	0·30	0·60	3·40	0·70	—	,,
Meissen hard paste porcelain (*dégourdi*), 1825	57·70	36·00	0·30	—	5·20	0·80	—	,,
Meissen hard paste porcelain (baked), 1825	59·40	32·60	—	—	5·50	0·40	—	,,
Chinese hard paste porcelain	70·50	20·70	0·50	0·10	6·00	0·80	—	Malaguti & Laurent
Bristol hard paste porcelain, 1775–80	62·92	33·16	1·28	—	2·64	—	—	Church
English soft paste porcelain, 1847	39·88	21·48	10·06	—	2·14	—	26·44	Cowper
,, ,, ,, ,, 1889	41·01	23·05	–	—	2·46	0·10	33·09	Author
English earthenware (cream colour), 1889	63·10	33·09	1·05	0·12	0·22	2·10	—	,,
English earthenware (granite), 1889	70·90	27·25	1·00	—	0·10	1·02	—	,,
English stoneware (Lambeth)	74·00	22·04	0·60	0·17	1·06	2·00	—	Salvetat
,, ,, (Wedgwood)	66·49	26·00	2·04	0·15	0·20	6·12(?)	—	,,
English red facing brick of good quality	51·01	36·90	0·24	2·01	—	9·98	—	Author
English firebrick of good quality	70·86	24·68	0·21	0·63	—	2·90	—	,,
Saggers used in Staffordshire	68·24	26·31	0·18	—	—	4·89	—	,,

Glazes and glazing.—It is well at the outset that the terms 'glaze' and 'enamel,' which are often confounded, should be fairly defined. A glaze is a *transparent* vitreous coating, while an enamel is an *opaque* semi-vitrified coating, applied to any kind of potteryware to render it impervious to liquids or to serve as a means of decoration. But glazes and enamels may be stained with various oxides so as to produce different colours. The distinction is, however, not a very profound one, for enamels are usually simple lead glazes rendered opaque by the addition of oxide of tin.

A good glaze should answer to the following properties—

1. It should be clear, brilliant, and thin, so as not to hide modelled work.

2. It should have such a suitability to and agreement with the body, both in composition and dilatability, as neither to chip off from the sharp edges of the body, nor to break up in minute cracks (crazes) upon its surface.

3. It must be hard enough to resist wear, especially if used for culinary purposes.

4. It should not be attacked by water or by acid vapours, and if used for culinary, domestic, or sanitary purposes should not be attackable by any acid, save hydrofluoric.

There are but two glazes in ordinary use which can be said to answer these conditions perfectly, and they are the salt glaze so extensively applied to stoneware, and the glaze of hard paste porcelain; though the glaze on the best English soft paste porcelain ranks but slightly below them in all respects. Most of the other glazes in common use are defective in one or more of these points; though such faultiness may not prevent them from serving most of the purposes for which a glaze is intended. The commonest, and at the same time the most vital, of these faults is what is known as 'crazing,' *i.e.* cracking or splitting of the glaze in all directions on the surface of the ware, owing to the different rate of dilatability for changes of temperature of the glaze and the body to which it is attached. These cracks, fine as they are, readily absorb fluids, and when they occur on pieces used for the purposes of the toilet or the table, become not only offensive, but are said to be positive sources of danger from the fatty or oily fluids they have absorbed, forming possible breeding grounds for bacteria (*v.* Encyclopédie Chimique, tome v., pp. 70–71).

During the last fifty years or so many glazes have been introduced, both in Continental countries and in England, containing a large proportion of oxide of lead, so as to render the production of a rich brilliant glaze possible without the cost and the difficulties of a high temperature of firing. So overcharged are many of the commoner glazes with lead, that they are readily attacked by the acids of food in cooking, and to such an alarming extent has this soft lead glazing grown, that the German Government has recently forbidden the use of a glaze on any article for domestic use which will not resist the action of strong boiling acetic acid. The reasons for the superiority of the glazes mentioned above is not far to seek; they accord so well in nature with the body to which they are applied, and they penetrate it to such a depth, as to become to a certain extent incorporated with it; the temperature required for their perfect formation too is so high that they possess a degree of hardness superior to that of many varieties of glass. The method of application of the glaze of porcelain has been already described. Before proceeding to the question of glazes in general a brief account of salt glazing is desirable.

For the salt glaze process only such pastes can be used as contain a considerable excess of silica, uncombined with alumina. When ware of this nature is fired in the kiln with free circulation of the flame and smoke among it, the most expeditious method of applying the glaze is to throw on to the fires at the termination of the biscuit-firing a quantity of wet salt, or it may be thrown directly into the oven. Vapours of common salt and water thus pass into the oven, and a mutual decomposition takes place between them, resulting in the formation of hydrochloric acid vapours and the liberation of soda, which immediately combines with the silica of the ware, with the formation of a coating of a hard insoluble soda glass upon the surface exposed to the action of the fumes. The following equations may be used to express the changes:—

$$(1)\ 2NaCl + H_2O = 2HCl + Na_2O.$$
$$(2)\ Na_2O + SiO_2 = Na_2O.SiO_2.$$

though the changes are probably more complicated than this, as the iron compounds in the paste undoubtedly play an active, though possibly intermediate, part in the process.

Glazes may be divided into the four following classes according to their composition:

1. Alkaline glazes (silicates of soda and potash). Ex. Salt glaze, Egyptian turquoise.
2. Felspathic glazes (silicates of the alkalis and alkaline earths). Ex. Glaze of hard porcelain and of some English porcelains.
3. Lead glazes (silicates and silico-borates of the alkalis and alkaline earths, softened by the addition of oxide of lead). Ex. All ordinary clear glazes for earthenwares and of most English porcelains.
4. Stanniferous glazes or enamels (as 3, but with oxide of tin, rendering them opaque). Ex. Opaque enamels for majolica, white bricks, &c.

Of the purely felspathic glazes it will be sufficient to state here their general composition, their methods of application and preparation resembling those shortly to be described. The different relationship in which they stand to the body has been already commented on in speaking of hard porcelain paste. The best of these glazes is now simply the ground pegmatite (containing mainly felspar and quartz) which is found associated with the kaolin used for the paste. A glaze in use at Berlin in 1836 had the following percentage composition: kaolin 31, quartz 43, gypsum 14, porcelain pitchers 12. The best English porcelain glazes are quite free from lead, but borax is added to the felspar to render it somewhat more fusible. One of the best English glazes is prepared as follows:—Fritt together 5 parts of China stone, 2 parts of boracic acid, 1 part of lime, and 1 part of flint, and then grind the fritt with 1½ parts of dried China clay.

The glazes of the third class are in very extensive use at the present time, and are of every degree of fusibility according to the purpose to which they are applied. In making glazes of this nature, a fritt or coarse glass is first made containing all the soluble materials, such as borax, soda, &c., together with such of the other ingredients as will enable them to form a well vitrified, insoluble glass. This glass or fritt is then weighed out, together with the requisite proportions of flint, china stone, white lead, or such other insoluble materials as are necessary, and the whole mixture is ground together on a pan similar to the one shown in fig. 1, until it is perfectly fine. The glaze in suspension in water is then put into convenient tubs, and the biscuit ware dipped in it; a portion of the water is absorbed; and a thin coating of powdery glaze is left on the piece. The articles are placed in saggers, being carefully supported on pointed supports—the saggers are piled in bungs in an oven such as those shown in fig. 3 or 4, and the whole is submitted to a second firing, less in intensity than the first or 'biscuit' firing, but sufficient to completely melt the glaze upon the surface of the ware. The older form of oven shown in fig. 4 answers better for glazing than the down-draught form shown in fig. 3, because in the latter form the fumes and products of combustion, being kept longer in the oven, are more likely to penetrate the saggers and damage the brilliance of the glaze. It is essential to lute the saggers together with a roll or 'wad' of clay for the 'glost' fire, to prevent the penetration of fumes into the saggers during the firing. With the softer kinds of glaze belonging to classes 3 and 4, such as are used for the decoration of English majolica, the pieces after dipping, instead of being inclosed in saggers, are all placed carefully in a kiln similar to the one shown in section in fig. 5. This kiln plays the part of one big sagger, and the flame playing all round it raises the kiln and its contents to a temperature sufficient for the fusion of glazes rich in lead such as are used for these purposes.

The following table gives the composition of a few typical lead glazes, from the harder ones used for bone china to the softer ones used for English majolica ware:—

—	Fritt							Glaze			
	Borax	Chalk	Flint	China stone	Felspar	Soda	Kaolin	Fritt	Flint	China stone	White lead
English china glaze	50	16	40	24	33	—	—	45	—	15	15
English earthenware glaze	48	38	62	—	—	26	30	230	60	160	120
English granite glaze	80	30	80	100	40	40	30	360	50	50	80
English majolica glaze	40	20	40	100	—	12	—	100	—	10	120
English parian glaze	20	—	15	20	—	—	5	20	—	—	64
English soft tile glaze	—	—	—	—	—	—	—	—	11	22	56

These recipes might be multiplied a hundredfold, but sufficient are here given to show the general lines of their composition, and represent glazes in actual use.

Coloured glazes.—In recent years a great variety of coloured glazes have been introduced, especially for the decoration of wall tiles. The basis of these glazes is in most cases a fritt rich in lead; and for the greens and blues derived from cupric oxide, a glaze with a base of silicate of soda and lime. In every case the object is to get a glaze with a rich, luscious appearance, and fusible at such a low heat as not to impair by volatilisation or otherwise the tone of colour produced by the addition of small quantities of oxide of iron, oxide of cobalt, oxide of manganese, &c. The following glaze is given by Salvetat in the Dictionnaire des Arts et Manuf., as the basis of a glaze suitable for producing a variety of coloured glazes and adaptable either to soft-paste porcelain, earthenware, or tile bodies:

Red lead	2,000 grammes.
Flint	1,000 ,,
Borate of lime	500 ,,

This forms a colourless fusible basis, and by the addition of the various colouring oxides to it any desired variety of shade can be produced.

Blues by the addition of from 40 to 125 grms. of CoO to the above quantity of glaze. Blue-greens by the addition of from 100 to 500 grms. of CuO to the above quantity of glaze. Ivory to strong yellow by the addition of from 70 to 200 grms. of Fe_2O_3 to the above quantity of glaze. Madder-brown to purple-brown by the addition of from 70 to 125 grms. of Mn_3O_4 to the above quantity of glaze, and various intermediate tints by admixture of the different oxides in various proportions.

The mixture of materials and colouring oxide after being ground coarsely together is melted in crucibles, and then poured out into water and ground fine; in this way a more perfect combination is obtained than by simply grinding the materials together. An English mixture serving the same purposes, but not quite so fusible nor so readily applicable to the various bodies as the one given above, is made by grinding together flint 100 parts, China stone 90 parts, red lead 360 parts, borax 40 parts; the mixture is fritted together in flinted saggers, ground, and then various proportions of finely ground metallic oxides added to it for colouring purposes. These glazes may be applied by dipping like ordinary glazes, but they are often applied with large camel-hair pencils, and by mingling them together in various ways beautiful effects of colour are readily obtained.

Turquoise glaze. This most rare and brilliant colour, brought to perfection by the ancient Egyptians, and made also by the Assyrians, has been recently investigated by Salvetat, who finds that the true turquoise blue is only developed by the solution of oxide of copper in a silicate of soda, and on a body rich in silica. He gives the following composition receipts for body and glaze:—

Body.		Glaze.		
Silica	93·0	Sand	900	Fritted together.
Alumina	4·0	$NaHCO_3$	400	
Lime	2·0	Chalk	100	
Potash	0·5	CuO	135	

Much attention has been devoted of late years by ceramic chemists in Europe to the composition of Oriental glazes and enamels—and the reader is referred to an article on p. 442 of vol. 5 of Fremy's Encyclopédie; to several added articles by Salvetat in the 1877 ed. of Brongniart's Arts Céramiques, and to various notices in the Chemiker-Zeitung for 1888–89.

The stanniferous glazes, or enamels as they are more generally called, are not so widely used now except for the manufacture of white glazed bricks as they were at the time of the Renaissance in Italy, when the famous Italian majolica and Della Robbia wares were decorated largely on a ground of opaque tin enamel. A revival of this manufacture has taken place in Italy, and both in that country and in France there are several factories for the production of faïence with a stanniferous glaze. The following receipts are given by Deck for the principal enamels of this class:—

White. Lead and tin ashes, 44; sand, 44; soda, 2; common salt, 8; red lead, 2.

Yellow. White as above, 91; oxide of antimony, 9.

Blue. White as above, 95; oxide of cobalt, 5.

Green. White as above, 95; cupric oxide, 5.

Yellow-green. White as above, 94; cupric oxide, 4; antimoniate of lead, 2.

Violet. White as above, 96; manganese dioxide, 4; though, of course, the exact composition of the glaze depends on the body to which it is to be applied.

Bodies very rich in fusible material, like Parian and some of the finer stonewares, become quite impervious to liquids, and acquire a smooth and glossy surface without the application of a glaze, from the semivitrification of the paste itself. Opener and less fusible bodies than these acquire a similar surface if they are fired in saggers, the insides of which have been washed with glaze rich in oxide of lead, and containing chlorides or fluorides. Mixtures of oxide of lead with cryolite, fluorspar, common salt, calcium chloride, &c., are the best for this purpose. When heated they probably give off volatile fluorides or chlorides of lead, and these are again decomposed on the surface of the ware, forming a thin smear or coating of silicate of lead.

Colours.—No department of pottery has made such advances during this century as the preparation of the various ceramic colours, and while at the beginning of the century the colours were for the most part fired *on* the glaze at low temperatures, we now possess coloured bodies, under-glaze colours, and on-glaze colours in abundance. Owing to the fact that all pottery colours require to be submitted to at least a red heat, no organic colours can be used for this purpose, and recourse must therefore be had to such inorganic compounds as will produce colour effects without decomposition at high temperatures, and under the action of alkaline glazes and fluxes. The list of substances which answer these requirements is by no means a large one, comprising only the oxides of cobalt, nickel, iron, manganese, zinc, copper, antimony, lead, uranium, and iridium, a few salts, such as the chromates of iron, lead, and barium, the natural ochres, purple of Cassius, and a few obscure compounds which will be described later. For the preparation and properties of each of these substances, reference must be made to the respective articles in this work in which they are treated at length.

Coloured pastes.—In almost every form of pottery belonging to classes 2 and 3, it is possible to stain the white pastes with various colours; but owing to the fact that they have to endure the most intense heat of the whole process, the number of colours is very limited. The pastes rich in fusible material, especially those rich in felspar, stain most beautifully, as the felspar forms a neutral flux in which the particles of colouring matter are dissolved, and so produce their richest effect. Mosaic tiles and tesseræ, coloured parians, porcelains, and jaspers, are the best examples of coloured pastes, and are all bodies rich in fusible materials. The following are a few of the proportions used:—

Blue (*pale*). 95 parts of paste; 5 parts of oxide of cobalt.

Blue (*strong*). 90 parts of paste; 10 parts of oxide of cobalt.

Green. 85 parts of paste; 5 parts of oxide of cobalt; 10 parts of oxide of chromium.

Blue-green. 95 parts of paste; $2\frac{1}{2}$ parts of oxide of chromium; $1\frac{1}{4}$ parts oxide of cobalt; $1\frac{1}{4}$ parts oxide of zinc.

Bronze-green. 95 parts of paste; 5 parts of calcined oxide of nickel.

Brown. 85 parts of paste; 15 parts of calcined oxide of iron.

Yellow. 90 parts of paste; 10 parts of oxide of titanium.

Black. 90 parts of paste; 7 parts of oxide of iron; 3 parts of oxide of cobalt.

In the decorative process known as barbotine or slip painting, colouring oxides are often added to ordinary earthenware or stoneware pastes, but the effect is much inferior in juicy richness unless the article be afterwards glazed.

Under-glaze colours.—These colours, consisting for the most part of oxides, chromates, or silicates, mixed with china clay, flint, &c., so as to diminish the action of the glaze upon them, or to assist in the development of the tone of colour required, are applied on the porous biscuit ware before the piece is glazed. They must therefore resist the action of the glaze at a temperature sufficient to melt the latter; they must be infusible enough to remain *still* under it; and they must have such an agreement with both the glaze and the body as not to cause the glaze to fly off in flakes. The following colours answer well for both china and earthenware:—

Black. 8 parts of native chromate of iron; 3 parts of Mn_3O_4; 3 parts of CoO; 1 part of flint, calcined together strongly and then ground fine.

Dark blue. 4 parts of CoO; 1 part of flint; 1 part of chalk, ground together.

Azure blue. 60 parts of ammonium-alum; 3 parts of oxide of cobalt, calcined strongly, then ground and washed thoroughly till free from traces of acid.

Blue-green. 12 parts of borax; 12 parts of chalk; 12 parts of oxide of zinc; 24 parts of green oxide of chromium; 4 parts of oxide of cobalt; calcine well together and grind till fine.

Dark brown. 8 parts of native chromate of iron; 4 parts of oxide of zinc; 2 parts of oxide of iron ground well together, calcined strongly and re-ground.

Red-brown. 6 parts of precipitated chromate of iron; 20 parts of oxide of zinc; 3 parts of litharge, calcine together strongly, and then grind till fine.

Pink colour. Oxide of tin, 100; chalk, 34; oxide of chromium (Cr_2O_3), 1; silica, 5; mixed well together, calcined strongly, and ground.

Yellow. Oxide of antimony, 3; red lead, 6; flint, 2; oxide of tin, 1; calcined together and then ground.

In all these colours the important point is to have the materials well ground together before calcining, in order that their union may be as intimate as possible; and the value of the tint is much improved if the final grinding be as perfect as possible.

On-glaze colours.—These colours are really fusible glasses, of such a nature that when they are applied upon the fired glaze, and the whole piece is then raised to a red heat, the coloured glasses fuse and adhere to the glaze. Unless this union with the glaze be very perfect, such colours are always liable to wear off, and they never have the richness of under-glaze colours owing to the much lower heat at which they are fired. On-glaze colours are divided into the two classes of regular-kiln colours (Fr., *couleurs de moufles tendres*), and hard-kiln colours (Fr., *couleurs de moufles dures*), the latter colours containing a smaller proportion of flux than the former and hence requiring a higher temperature of firing.

The first requisite in the preparation of on-glaze colours is a series of fluxes which shall accord well with the glaze on which they are to be fired, shall fuse at a sufficiently low temperature, and shall dissolve the particles of colouring matter without decomposition. Salvetat has prepared a series of fluxes which answer perfectly for hard-paste porcelain. Their composition is as follows:—

—	No. 1 Flux	No. 2 Flux	No. 3 Flux	No. 4 Flux	No. 5 Flux
Litharge . .	75	66·66	11·12	37·50	73·00
Silica . . .	25	22·22	33·33	12·50	9·00
Calcined borax .	—	11·11	55·55	-	—
Boracic acid .	—	—	—	50·00	18·00

No. 1 is a special flux for certain dark blues fired in the hard kiln; No. 2 is the general flux for browns, greys, yellows, and iron-reds; No. 3 is the flux for carmines made from gold, and No. 4 for gold purples; No. 5 is the peculiar compound used for greens prepared from oxide of chromium—a flux used for a similar purpose at Meissen is composed of 73 parts of litharge, 18 parts of silica, and 9 parts of boracic acid.

The fluxes used in England differ considerably from the foregoing on account of the different nature of the glazes to which they are applied; in this country almost every colourmaker has fluxes of his own, and there is considerable difficulty in arriving at anything like a general statement as to the composition of the fluxes used. The following compositions are for fluxes largely used in Staffordshire:—

—	No. 1 Flux	No. 2 Flux	No. 3 Flux	No. 4 Flux	No. 5 Flux
Red lead . .	64·50	49·99	30·55	15·76	40·00
Silica . . .	21·50	16·66	41·68	21·19	20·00
Borax (cryst.)	–	33·33	27·77	63·05	40·00
Flint glass . .	14·00	—	—	-	–

No. 1 is a special flux for a brilliant scarlet prepared from lead bichromate: and the remainder are used for the same purposes as the similarly numbered French fluxes described before.

The preparation of all the fluxes is as follows. The various ingredients are carefully ground together dry, and then melted in good crucibles; when thoroughly melted they are poured out either into water or on to a slab, the latter method being preferable, as fluxes rich in borax are somewhat easily attacked by water. They are then ground to a fine powder, and are ready for mixing with the colouring agent.

The following typical mixtures are given as an indication of the general composition of on-glaze colours; the proportions of colour and flux remain good in all cases, the only point being to use a suitable flux:—

Regular-kiln colours (*couleurs de moufles tendres*):

Strong grey. Flux No. 2, 68 parts; carbonate of cobalt, 6; ferric hydrate, 13; zinc carbonate, 13.

Pale grey. Flux No. 2, 92 parts; carbonate of cobalt, 5; ferric hydrate, 3.

Strong black. Flux No. 2, 80 parts; carbonate of cobalt, 10; ferric hydrate, 10.

Iridium black. Flux No. 2, 75 parts; sesquioxide of iridium, 25.

Uranium black. Flux No. 2, 75 parts; black oxide of uranium, 25.

Strong blue. Flux No. 2, 61 parts; carbonate of cobalt, 13; carbonate of zinc, 26.

Pale blue. Flux No. 2, 80 parts; carbonate of cobalt, 6; oxide of zinc, 14.

Blue-green. Flux No. 5, 75 parts; carbonate of cobalt, 6; green oxide of chromium, 19.

Sea-green. Flux No. 2, 80 parts; carbonate of copper, 20.

Pale yellow. Flux No. 1, 80 parts; antimoniate of potash, 14; carbonate of zinc, 6.

Orange. Flux No. 1, 80 parts; antimoniate of potash, 14; red oxide of iron, 6.

Uranium orange. Flux No. 1, 75 parts; yellow oxide of uranium, 25.

Yellow brown. Flux No. 2, 75 parts; ferric oxide, 10; carbonate of zinc, 15.

Red. Flux No. 2, 75 parts; red ferric oxide, 25.

Rose colour. Flux No. 3, 87 parts; purple of Cassius, 12; precipitated silver, 1.

Purple. Flux No. 4, 90 parts; purple of Cassius, 7; oxide of gold, 3.

All these colours, with the exception of the last three, are made by grinding together the constituents, then fusing the mixture in crucibles, and regrinding perfectly fine. Of the remaining three colours, the red from oxide of iron needs most careful preparation. The oxide for this purpose is prepared by carefully calcining dried ferrous sulphate until the brilliant red tint is fully developed, which takes place between 400–420°C. Below this temperature a dirty yellowish brown, and above it a dark purplish brown product, is obtained. The oxide of iron and flux are simply ground together, not calcined.

The colours prepared from gold are obtained by mixing the ingredients well together, and submitting the mass to a gentle calcining at a temperature below redness; they vary in tint with the degree of heat to which they are subjected, changing from a full rose colour at a clear red heat to a dullish purple at a heat approaching whiteness.

Hard-kiln colours (*couleurs de moufle dures*). These colours are prepared from materials similar to those used for regular kiln colours, but they contain a smaller proportion of flux. Owing to the greater heat to which they are subjected, the number of compounds which can be used is rather more limited than in the former case, but the colours become so fused into the glaze that they attain an added richness and brilliancy, and at the same time gold and other metals can be applied on them for decorative purposes.

Metals.—Only the noble metals can be used in the metallic state for the decoration of pottery, and of these only gold, silver, and platinum are in actual use. The preparation of the gold for pottery purposes necessitates its production in as fine a state of subdivision as possible. Two methods are in use for this purpose:

1. The French method; in which the gold is obtained in a finely-divided state by precipitating a very dilute solution of the chloride with a dilute solution of ferrous sulphate (*v.* art. GOLD). The precipitated gold, after very careful and often repeated washings, is dried and well ground with $\frac{1}{12}$th of its weight of subnitrate of bismuth or of calcined borax; this powder is then made up into a pigment by mixing it with oil of lavender or fat turpentine, and when fired the subnitrate of bismuth or the borax serves to flux it on to the glaze.

2. The English method; by which an amalgam of equal parts of gold and mercury is prepared, mixed with $\frac{1}{10}$th to $\frac{1}{12}$th of its weight of the No. 2 Flux given above, and ground under water to an impalpable powder. This is dried, mixed with fat oils, and applied, like the other, and when fired the mercury volatilises leaving the gold with a dead or matt surface, which is then brightened by scouring with sand and burnishing with agate. Silver and platinum are seldom used by themselves, but by adding from $\frac{1}{4}$ to $\frac{1}{2}$th of them to the gold, light and green golds are produced, which are much prized as decorative adjuncts to the ordinary gold.

For very elaborate and expensive work, gold is sometimes prepared by grinding gold-leaf under water with the requisite amount of flux. The powder thus obtained is then dried, and ground up with clear honey to a workable consistency. It is applied thickly, and after firing can be chased and cut up with agate chasers.

Quite recently Mr. W. De Morgan, of Chelsea, and Messrs. Maw, of Broseley, Salop, have revived the lustre decorations which were carried to such a pitch of perfection by the Moors during their occupation of Spain, especially about the twelfth century. The lustre pigments, containing compounds of silver and copper as colouring agents, are applied on the fired glaze or enamel, and are then again raised to a red heat in a kiln so contrived that when this temperature has been reached a large volume of smoke from burning brushwood is passed into the kiln. The copper compounds are reduced to the lower stage of oxidation, giving a rich red background of colour, on which an iridescent film of metallic copper or silver may be also at the same time produced. The effects obtained are singularly rich and beautiful, and it is to be hoped, for the sake of the art, that the process may be commercially successful.

Application of colours.—The colours are applied by printing or by painting. In each case the colour is mixed with a resinous medium to give it body. For printing purposes it is made up into a kind of ink or pigment by mixing it with thick, boiled linseed oil. The mixture is then worked into an engraving or etching on a flat copper plate; the excess of colour removed, and a print taken from the engraving on to thin tissue paper. The paper print is then applied to the required article; in the case of under-glaze colours on the biscuit ware, and in the case of the on-glaze colours on the glazed ware. The porous biscuit ware readily absorbs the colour from the paper, which can then be washed off; the glazed pieces are first 'primed' with a size made by thinning down Canada balsam with turpentine; this size serves to absorb the colour, and after standing some time the paper can also be washed off in this case, leaving behind a perfect impression in colour. The ware then requires to be fired, and this firing is effected in a closed kiln or muffle, shown in section in Fig. 5. The ware is carefully piled in this; in the case of biscuit ware it is heated to full redness to expel the printing oils, and leave the ware in a condition to receive the glaze; in the case of on-glaze colours the firing is carefully regulated to suit the particular colours in question.

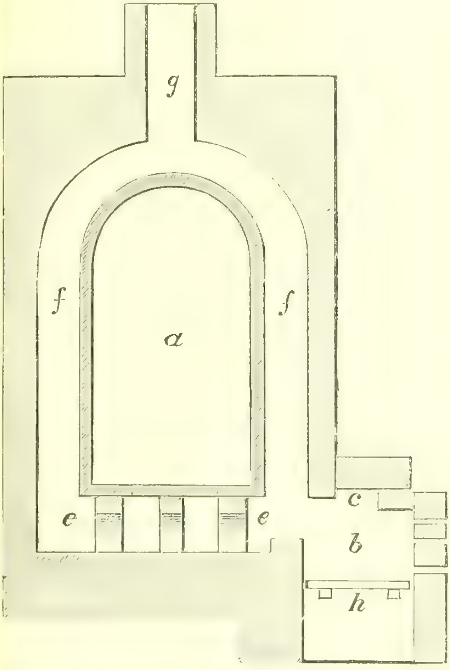


FIG. 5.—TRANSVERSE SECTION OF ENAMELLING KILN.

a. Kiln. *b.* Fireplace, charged at *c.* *e.* Bottom flue. *f.* Upright flues. *g.* Chimney.

In painting, the colours whether under-glaze or on-glaze, are mixed up into workable pigments with fat turpentine, oil of lavender, aniseed, &c., and applied with camel-hair pencils in the ordinary way.

Metals are usually fluxed, so as to adhere perfectly to the glaze at the heat necessary to fire up the on-glaze colours.

Many pyrometers have been proposed for pottery purposes, but in practical work the fireman always judges of the progress of the firing by small trials of a similar substance to the material being fired, and which he removes from the oven or kiln from time to time by holes specially left for the purpose.

Literature.—For all details connected with the practical work, Brongniart's great work Traité des Arts Céramiques, especially the edition of 1877 with additions by Salvetat, is the best book, and is especially good in its account of the manufacture of hard porcelain, though meagre in its accounts of English bodies and processes. Several works by Salvetat are of importance, notably his Leçons de Céramique. Alex. Martin, Faïences et Porcelaines. Th. Deck, La Faïence, 1887. Vol. 5 of Fremy's Encyclopédie Chimique may be looked on as a modernised Brongniart confined to hard-paste porcelain. There is no good work in English on the subject; the best information, and for the most part reliable, is to be found in the catalogue of the collection of pottery in Jermyn Street Museum, and the book contains a valuable appendix by Geo. Maw, Esq., one of the foremost potters in the country, on the Clays and Plastic Strata of Great Britain. W. B.

POZZUOLANA *v.* CEMENTS.

PRASEODYMIUM *v.* CERIUM METALS.

PRECIPITATE, RED, *v.* MERCURY.

PRECIPITATE, WHITE, *v.* MERCURY.

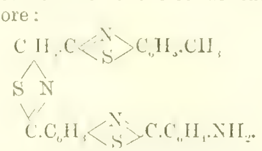
PREHNITENE *v.* CYMENES.

PRIMROSE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PRIMULINE *v.* AZO-COLOURING MATTERS (vol. i., p. 224). Further particulars respecting the constitution of this colouring matter have been made known since the article above referred to was written. The thio- base, which is made by heating sulphur and paratoluidine, consists of a mixture of dehydrothiotoluidine (amidobenzenyl-*p*-*m*-amidothiocresol) and a condensation product formed by the coalescence of two molecules of the latter compound with the elimination of hydrogen sulphide. The condensation is brought about by the further action of sulphur:

$$2C_{14}H_{12}N_2S + 2S_2 = C_{28}H_{18}N_4S_3 + 3H_2S.$$

The constitution of the condensation product is therefore:


C H$_3$.C<^N_S>C$_6$H$_3$.CH$_3$
S N
C.C$_6$H$_3$<^N_S>C.C$_6$H$_4$.NH$_2$.

It is the sulphonic acid of this last base which has the affinity for cotton fibre which renders it so valuable for the production of 'ingrain' colours by diazotising in the fibre and then combining with phenols, &c. The dehydrothiotoluidine has no affinity for vegetable fibre, and is thus lost in the bath after the 'primuline' sulphonic acid has been taken up.

The commercial product is the sodium salt. It dissolves in strong sulphuric acid without colour, the solution having a blue fluorescence and giving a yellow flocculent precipitate on dilution. The aqueous solution is yellow, giving a dark-yellow flocculent precipitate of the free acid on adding hydrochloric acid. Alkalis throw down a light-yellow flocculent precipitate. Cotton dyed with primuline is of a pale sulphur-yellow colour, which becomes redder on wetting with hydrochloric acid, and is restored to the original colour on washing with water.

Diazotised primuline on organic fabrics undergoes decomposition on exposure to light; this property has been utilised for the production of photographic prints by the 'diazotype' process (Green, Cross & Bevan, S. C. I. 1890, 1001), *v.* Photography. R. M.

PRINCE'S METAL or **PRINCE RUPERT'S METAL.** A brass containing about 25 p.c. of zinc.

PRINTER'S IRON LIQUOR. *Ferrous acetate v.* Acetic acid.

PRODUCER GAS *v.* Fuel.

PROOF SPIRIT *v.* Alcohol.

PROPIOLIC ACID *v.* Indigo.

PROPIONIC ACID *v.* Fatty acids.

PROPYL ACETIC ACID. *Valeric acid v.* Fatty acids.

PROPYLBENZENE *v.* Cumenes.

PROPYLPYROGALLOL *v.* Phenol and its homologues.

PROTEÏDS *v.* Albuminoids.

PROTEIN *v.* Albuminoids.

PROTOCATECHUIC ACID *v.* Hydroxy- acids.

PROUSTITE. *Light-red silver ore.* A silver sulpharsenite, Ag_3AsS_3 or $3Ag_2S.AsS_3$ (Rose), found in rhombohedral crystals H = 2–2·5, sp.gr. 5·42–5·56. Lustre adamantine. Colour and streak, cochineal-red. Subtransparent to subtranslucent. Before the blow-pipe evolves arsenic, and on charcoal leaves metallic silver. Soluble in nitric acid. Found at Johanngeorgenstadt, Marienberg, and Annaberg, in Saxony; at Joachimsthal, in Bohemia; Wolfach, in Baden; Markirchen, in Alsace; Chalanches, in Dauphiné; Guadalcanal, in Spain; also in Mexico and Peru.

PRUNE *v.* Oxazine colouring matters.

PRUSSIAN BLUE *v.* Cyanides.

PRUSSIAN BROWN *v.* Pigments.

PRUSSIAN RED or **VENETIAN RED** *v.* Pigments.

PRUSSIATE OF POTASH *v.* Cyanides.

PRUSSIC ACID *v.* Cyanides.

PSEUDOCUMENE *v.* Cumenes.

PSEUDOCUMENOLS *v.* Phenol and its homologues.

PSILOMELANE. *Amorphous manganese dioxide v.* Manganese.

PSITACINITE *v.* Vanadium.

PTERITANNIC ACID *v.* Filix mas.

PTOMAÏNES *v.* Fermentation.

PUCHERITE *v.* Vanadium.

PUMICE STONE. A lava-froth formed from the glassy species of the acid lavas when distended during their period of fusion by the escape of steam. The solid volcanic products are divided into two classes, distinguished as the glassy and the crystalline, of which the latter consists of a mass of crystals floating in a liquid base: the former presenting a more perfectly-fused appearance. Jets of steam forcing their way through the crystalline form produce scoria or cindery material; whilst pumice is the form assumed by the action of the water vapour on the glassy form. It is, in fact, a mass of glass globules, which, however, usually present an elongated and sometimes ruptured form by reason of the movement of the lava stream. In consequence of its being permeated with air-chambers, pumice floats upon the water for some time; and after a period of volcanic activity it has been known to seriously impede the progress of vessels by its quantity in the seas adjacent to excited craters. Recent deep-sea soundings show the bottom of the ocean far from land to be covered with particles of pumice and scoria which must have floated thither. Pumice stone itself is specifically heavier than water, and sinks immediately if powdered. Its silky fibres present a characteristic vitreous whiteness due to the reflection of a portion of the light in its rapid interchange from the medium of air to that of glass and *vice versâ.* The analysis of pumice does not materially differ from that of the more compact mass. (*V.* Lava.)

PUNICIN. The name given by Schunck to the colouring matter formed from *Purpura capillus* and other shell-fish used by the ancients in the dyeing of linen and woollen fabrics. From the observations of Cole (Tr. 1685), Réaumur (Mem. de l'Acad. Royale des Sciences, 1711), and Bancroft (Philosophy of Permanent Colours, 1, 120, 1803), it appears that the colour-producing secretion, which resembles pus in appearance and consistence, is contained in a small whitish cyst or vein, placed transversely under, but in immediate contact with, the shell, and near the head of the animal. This pus-like matter, either diluted with water or undiluted, on being applied to bits of white linen or calico and exposed to sunlight rapidly changes its colour, passing from yellow, through light green, deep green, and 'watchet blue,' to purplish red or crimson. While these changes are in progress a strong odour, like that of garlic or asafœtida, is given off. To produce this change of colour the light of the sun is essential. It is effected more rapidly by the direct action of the sun's rays than by that of diffused light, but it does not take place in moonlight or in artificial light. If the linen or other fabric to which the secretion has been applied is kept in the dark, it remains unchanged, but when exposed to the sun it becomes purple, even after the lapse of years, though a little more slowly than at first. The metamorphosis which the change of colour indicates is not sensibly promoted by heat. It proceeds in a vacuum and in hydrogen or nitrogen gas as speedily as in air on exposure to light. The colour produced is remarkably stable, resisting the action of soap, alkalis, and most acids, being destroyed only by nitric acid and chlorine. (See also Bizis, Journ. de Ch. Med. 10, 99 (1835), and A. and G. de Negri, Gazz. Chim. Ital. 1875, p. 437). For details concerning the chromogen of *Purpura capillus v.*

Schunck, C. J. 35 (1879), p. 591. Schunck finds that the colouring matter (punicin) is quite insoluble in water, alcohol, and ether, and sparingly soluble in boiling benzene and boiling glacial acetic acid, and readily soluble in boiling aniline, giving a solution which is at first green, but as it approaches saturation becomes purplish-blue. At this point it shows a broad, well-defined absorption band, beginning near C and extending beyond D; but, as the solution cools, depositing the substance contained in it, the colour changes to green, and the band becomes gradually narrower, until it occupies the space midway between C and D, and it then disappears. The masses of colouring matter deposited from the solution in aniline are seen, under the microscope, to consist of star-shaped groups of irregular crystalline needles, which, when very thin, show by transmitted light a purple colour. Punicin is soluble in oil of vitriol, giving a dirty purple colour, and showing a broad ill-defined absorption-band between D and E, the green and blue of the spectrum being much darkened. On heating the solution slightly, or allowing it to stand for some time, the colour changes to a bright bluish-green, and it now shows an absorption-band in the red. Punicin is also sparingly dissolved by a hot alkaline solution of stannous oxide, and the solution on exposure to air becomes covered with a blue pellicle. Punicin may be sublimed, giving crystals which show by reflected light a semi-metallic lustre, like that of sublimed indigo-blue (Schunck, *l.c.*).

PURPLE OF CASSIUS *v.* GOLD PURPLE.

PURPLE OF MOLLUSCA *v.* PUNICIN.

PURPLE, HESSIAN, *v.* AZO- COLOURING MATTERS.

PURPLE OCHRE (*Mars violet*) *v.* PIGMENTS.

PURPURIC ACID. $C_8H_5N_5O_6$. An acid obtained by the action of nitric acid upon uric acid. Its acid ammonium salt is *Murexide*,

$$C_8H_4N_5O_6NH_4.H_2O,$$

(*q. v.*). Free purpuric acid is a very unstable body. On treating a purpurate with an acid the purpuric acid is at once decomposed into dialuramide and alloxan

$$C_8H_5N_5O_6 + H_2O = C_4H_5N_3O_3 + C_4H_2N_2O_4$$

(Beilstein, A. 107, 176).

PURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

PURPUROGALLOL *v.* *Pyrogallol,* art. PHENOL AND ITS HOMOLOGUES.

PURPUROXANTHIN (1, 3) *Dioxyanthraquinone* *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

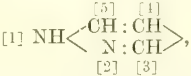
PURREE, PIURI, or **PIOURY,** *v.* EUXANTHON and INDIAN YELLOW.

PUTRESCINE *v.* FERMENTATION.

PUTTY POWDER. *Stannic oxide.* Common qualities of putty powder are produced by skimming the surface of boiling tin, the scum so obtained being then freed from foreign matter and well washed and ground. The better kinds are obtained by treating tin with nitric acid, thus forming stannic oxide. It is used in enamelling to give an opaque white colour; it is also employed for polishing. (*V.* TIN SALTS AND OXIDES.)

PYRARGYRITE (*Silver sulphantimonite*) *v.* ANTIMONY.

PYRAZOLE $C_3H_4N_2$ or $NH<\begin{smallmatrix}CH:CH\\N:CH\end{smallmatrix}>$, an isomeride of glyoxaline or imidazole, has been prepared by Buchner (B. 22, 2165), and later by Balbiano (B. 23, 1103). Prior to its synthesis, however, phenylderivatives of pyrazole and of ketodihydropyrazole, or *pyrazolone* $NH<\begin{smallmatrix}CO.CH_2\\N.CH\end{smallmatrix}>$, had been prepared by Knorr, Claisen, and others, by the action of phenylhydrazine or its homologues on either β-diketones or β-ketocarboxylic acids respectively.[1] To indicate, in the case of these compounds, the orientation of the radicles in the pyrazole 'ring,' Knorr proposed the following scheme:



$$[1]\ NH<\begin{smallmatrix}\overset{[5]}{CH}:\overset{[4]}{CH}\\ \underset{[2]}{N}:\underset{[3]}{CH}\end{smallmatrix}>,$$

and, in accordance with it, a compound having the constitution $NPh<\begin{smallmatrix}CH:CH\\N:CMe\end{smallmatrix}>$ is known as 1:3-phenylmethylpyrazole.

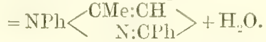
Pyrazoles.

For the preparation of pyrazoles the following methods have been described:—

(1) β-Diketones of the general formula R.CO.CHR′.CO.R″ (where R, R′, R″ are positive or negative radicles) react with primary aromatic hydrazines forming hydrazones, which readily undergo further condensation with the production of pyrazole derivatives (Knorr, A. 238, 139). Thus 1:3:5-diphenylmethylpyrazole is formed by the action of phenylhydrazine on benzoylacetone:

(*a*) $NHPh.NH_2 + COPh.CH_2.COMe$
$= NHPh.N:CPh.CH_2.COMe + H_2O$

(*b*) $NHPh.N:CPh.CH_2.COMe$



$$= NPh<\begin{smallmatrix}CMe:CH\\N:CPh\end{smallmatrix}> + H_2O.$$

Should R, R′, or R″ be a radicle containing carboxyl, a pyrazolecarboxylic acid is formed, which when heated loses carbon dioxide with the elimination of the carboxyl group and formation of the corresponding pyrazole. According to the Farbw. vorm. Meister, Lucius & Brüning (Germ. Pat. 33536, of Dec. 13, 1884; *cf.* Knorr and Blank, B. 18, 311, 2256; Claisen and Roosen, B. 24, 1890), ethylic benzoylacetoacetate yields ethylic diphenylmethylpyrazolecarboxylate (m.p. = 121–122°) by simple admixture with an equivalent proportion of phenylhydrazine, sufficient heat being evolved to bring about the complete condensation. On boiling with alcoholic potash this is readily converted into the acid, $C_{16}H_{13}N_2.COOH$ (m.p. = 205°), which when heated at 240–250° loses carbon dioxide and yields 1:3:5-diphenylmethylpyrazole. Homologues of phenylhydrazine or ethylic ortho- or para-nitrobenzoylacetoacetate can be employed in the reaction, and yield corresponding pyrazoles.

(2) Many unsaturated ketones or aldehydes having the general formulæ R.CO.CR′:CHR″ or HCO.CR.CHR′ respectively yield either pyrazole- or pyrazoline- derivatives or mixtures of

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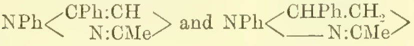
[1] Among the papers and patents relating to the preparation of β-diketones and β-ketocarboxylic acids are the following: Pechmann, Ber. 17, 2542; Claisen and Lowman, Ber. 20, 651, 655; Beyer and Claisen, B. 20, 2178; Claisen and Fischer, B. 20, 2191; Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 32245, 40747, 43847, and 49542.

both, when the hydrazones formed by condensation with primary aromatic hydrazines are distilled. Thus the hydrazone of benzalacetone yields on distillation a mixture of 1:5:3-diphenylmethyl-pyrazole and -pyrazoline—that is, NHPh.N:CMe.CH:CHPh yields a mixture of



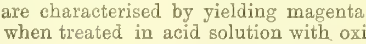
$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{CPh{:}CH}\\ \mathrm{N{:}CMe}\end{array}{>} \text{ and } \mathrm{NPh}{<}\begin{array}{l}\mathrm{CHPh.CH_2}\\ \mathrm{N{:}CMe}\end{array}{>}$$

(Knorr, A. 238, 141; B. 20, 1100). As before, when R′ is a radicle containing carboxyl, a pyrazolecarboxylic acid results, from which the corresponding pyrazole can be obtained by the elimination of carbon dioxide. For example, ethylic benzalacetoacetate and phenylhydrazine react in the cold with the formation of ethylic diphenylmethylpyrazolecarboxylate from which 1:5:3- diphenylmethylpyrazole can be obtained by saponification and elimination of carbon dioxide (Knorr and Blank, B. 18, 931; Knorr, B. 20, 1097).

Phenylpyrazole (Balbiano, G. 17, 176; 19, 128) and its homologues are insoluble in water but dissolve in the ordinary organic solvents. They are feeble bases, and their salts are decomposed by water. On treatment with sodium in boiling alcoholic solution they are readily reduced to the corresponding dihydropyrazoles or *pyrazolines*, which are likewise feeble bases, and are characterised by yielding magenta-red dyes when treated in acid solution with oxidising agents such as ferric chloride, nitrous acid, chromic acid, &c. This constitutes Knorr's pyrazole reaction (A. 238, 200 footnote).

Pyrazolones.

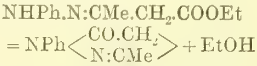
Inasmuch as two isomeric pyrazolones are theoretically possible, whose formulæ are



$$\mathrm{NH}{<}\begin{array}{l}\mathrm{CH{:}CH}\\ \mathrm{NH.CO}\end{array}{>} \text{ and } \mathrm{NH}{<}\begin{array}{l}\mathrm{CO.CH_2}\\ \mathrm{N.CH}\end{array}{>}$$

respectively, it is conceivable that derivatives of both these bases might be prepared. With the exception, however, of one case not yet fully established (Knorr, B. 20, 1107), all the oxypyrazoles hitherto obtained have been derivatives of the base 5-pyrazolone, having the latter formula, and these alone will be considered here.

5-Pyrazolone derivatives are formed if, in the methods just described for the preparation of pyrazoles, either β-ketonic acids are employed instead of β-diketones, or unsaturated acids are substituted for the corresponding unsaturated ketones or aldehydes (Knorr, A. 238, 141). Thus the hydrazone of ethylic acetoacetate when heated at 100° for some time yields 1:3-phenylmethyl-5-pyrazolone:—



$$\mathrm{NHPh.N{:}CMe.CH_2.COOEt}$$
$$= \mathrm{NPh}{<}\begin{array}{l}\mathrm{CO.CH_2}\\ \mathrm{N{:}CMe}\end{array}{>} + \mathrm{EtOH}$$

The following 5-pyrazolones, among others, have been described:—

1:3-Diphenylpyrazolone.

Preparation.—This base is formed when molecular quantities of phenylhydrazine and ethylic benzoylacetate are mixed together; heat is evolved in the reaction, and the product is separated in a crystalline form by the addition of ether.

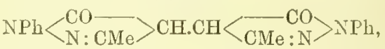
Properties.—1:3-Diphenylpyrazolone melts at 127°, is very sparingly soluble in water, sparingly soluble in ether and petroleum spirit, readily soluble in alcohol, chloroform, benzene, &c., and has both basic and feebly acid properties. When heated in sealed tubes at 100° with methyl iodide and methyl alcohol it yields *diphenylmethylpyrazolone*, which melts at 150°, is sparingly soluble in water, ether, and petroleum spirit, readily soluble in alcohol, and has feebly basic properties, differing in this respect from antipyrine, although both compounds are considered by Knorr to have an analogous constitution (Farbw. M., L. & B., Germ. Pat. 42726, of Aug. 7, 1887; Knorr and Klotz, B. 20, 2545).

1:3-Phenylmethylpyrazolone. *Methyloxyquinizine.*

Preparation.—(1) Molecular proportions of phenylhydrazine and ethylic acetoacetate are mixed together, and the oily hydrazone, after separation from the water formed in the reaction, is heated at 100° until a test becomes solid on cooling. The product, whilst still warm, is poured into ether, and the crystalline mass after washing with ether is dried at 100°. The yield is almost quantitative, but is dependent on the presence of exactly equivalent quantities of the two compounds, since excess of either leads to further condensation, and the production of complicated products (Knorr, Germ. Pat. 26429, of July 22, 1883; B. 16, 2597; 17, 546, 2032; A. 238, 147).

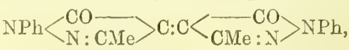
(2) Equivalent quantities of the anilide, toluidide, or naphthalide of ethylic acetoacetate and phenylhydrazine are heated for some hours at 150–200°, and the pyrazolone is extracted from the melt by means of aqueous soda (Farbw. M., L. & B., Germ. Pat. 41936, of Feb. 23, 1887; Knorr, A. 238, 146).

Properties.—It is crystalline, melts at 127°, boils at 287° under 265 mm. pressure, but decomposes when distilled at the ordinary pressure, and is slightly volatile with steam. It has both acid and basic properties, dissolves in alcohol and water, and on reduction with zinc-dust yields 1:3-*phenylmethylpyrazole.* When boiled with excess of phenylhydrazine it is converted into *bis-phenylmethylpyrazolone*,



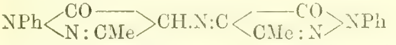
$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO}\\ \mathrm{N:CMe}\end{array}{>}\mathrm{CH.CH}{<}\begin{array}{r}\mathrm{CO}\\ \mathrm{CMe:N}\end{array}{>}\mathrm{NPh},$$

which, on oxidation with ferric chloride, platinic chloride, bromine water, nitrous and nitric acids, &c., is characterised by yielding *pyrazole-blue*



$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO}\\ \mathrm{N:CMe}\end{array}{>}\mathrm{C{:}C}{<}\begin{array}{r}\mathrm{CO}\\ \mathrm{CMe:N}\end{array}{>}\mathrm{NPh},$$

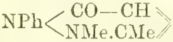
a colouring matter which in its constitution and in many of its properties closely resembles indigo-blue, but from which it is distinguished by its instability and lack of tinctorial power. Phenylmethylpyrazolone readily yields condensation compounds with aldehydes and ketones, and these, like the indogenides of the indigo series, are coloured yellow to red. A large number of derivatives of phenylmethylpyrazolone have also been prepared by displacing the hydrogen atoms of the methylene group by various radicles, and these serve to bring out the analogy between the pyrazolones and members of the uric acid series. Thus phenylmethylpyrazolone, like barbituric acid, yields an isonitroso-, a nitro-, and an amido- derivative, forming the violuric acid, the dilituric acid and the uramil of the series, whilst *rubazonic acid*,



$$NPh<\begin{matrix}CO——\\N:CMe\end{matrix}>CH.N:C<\begin{matrix}——CO\\CMe:N\end{matrix}>NPh$$

obtained by the oxidation of the amido- derivative forms its purpuric acid (Knorr, A. 238, 167 et seq.) The most important derivative of phenylmethylpyrazolone, however, is

Antipyrine. *Phenyldimethylpyrazolone*



$$NPh<\begin{matrix}CO—CH\\NMe.CMe\end{matrix}>$$, [(?), *cf.* Nef, A. 258, 267].

Preparation.—(1) Antipyrine is readily obtained by heating a mixture of equal parts of 1:3-phenylmethylpyrazolone, methyl iodide and methyl alcohol in closed tubes at 100° (Knorr, Germ. Pat. 26429 of July 22, 1883).

(2) Equivalent quantities of ethylic acetoacetate and symmetrical methylphenylhydrazine are heated in an oil bath at 140° until water and alcohol are no longer evolved; the antipyrine formed is then extracted from the melt by hot water. The yield is poor (Farbw. M., L. & B., Germ. Pat. 40377 of Nov. 4, 1886; Knorr, A. 238, 203).

(3) The ethylic phenylmethylpyrazolonecarboxylate (m.p. = 134°) resulting from the condensation of phenylhydrazine with ethylic acetonedicarboxylate is heated with methyl iodide and methyl alcohol in the usual way; antipyrine is then obtained from the product by first saponifying and then heating to eliminate carbon dioxide (Farbw. M., L. & B., Germ. Pat. 32277 of Nov. 25, 1884).

Properties. — Antipyrine crystallises in lustrous triclinic forms, melts at 113°, and dissolves in one part of water, two parts of absolute alcohol, $1\frac{1}{2}$ parts of chloroform, and 50 parts of ether at 12° (Gay and Fortuné, J. Pharm. et Chim. [5] 17, 594); it is also readily soluble in benzene. Unlike 1:3-phenylmethylpyrazolone it is a strong monacid base, yielding salts which dissolve readily in water but do not in general crystallise well. Antipyrine has been largely used as an antipyretic in doses of 0·3 to 1 gram, the decline of febrile heat commencing within a few minutes after the administration of the drug, and persisting for from one to sixteen hours, according to circumstances. It is not, however, an anti-periodic (Knorr, Ber. 17, 2037 footnote). In aqueous solution, antipyrine gives a red colouration with ferric chloride, whereby one part in 100,000 can be detected. It further gives with nitrous acid, after a few seconds, a pure blue-green colour in dilute, and a green crystalline precipitate in concentrated, solutions, whereby one part in 10,000 can be detected (Knorr, B. 17, 549; Smith, S. C. I. 1886, 580).

Note on the constitution of antipyrine.—The marked difference in the basic properties of antipyrine and 1:3-phenylmethylpyrazolone seems difficult to account for if the formula assigned by Knorr to the former is correct. It is conceivable, in view of the analogy between pyrazolone- and indole- derivatives, that the action of methyl iodide and methyl alcohol on 1:3-phenylmethylpyrazolone results in the formation of a six-membered 'ring' containing four carbon atoms, just as it leads to the production of a quinoline- derivative in the case of methylketole (Fischer and Steche, B. 20, 818, 2199).

Phenylantipyrine (*diphenylmethylpyrazolone*) has been prepared by the action of hydrazobenzene on either ethylic acetoacetate or ethylic acetonedicarboxylate. It does not, however, appear to have found any use in medicine (Gesellsch. für Chem. Ind., Germ. Pats. 39563, 39564; Müller, B. 19, 1771; Perger, B. 19, 2140). W. P. W.

PYRENE *v.* Wood, distillation of.

PYRETHRIN *v.* *Pellitory resin*, art. Resins.

PYRETHRINE *v.* Resins.

PYRETHRIC ACID *v.* Resins.

PYRIDINE *v.* Bone oil.

PYRITES, COPPER, *v.* Copper.

PYRITES, IRON, *v.* Iron; Sulphuric acid.

PYROACETIC ACID *v.* Acetic acid.

PYROCATECHIN, PYROCATECHOL, *v.* Phenol and its homologues.

PYROCHLORE *v.* Niobium.

PYROCOLL *v.* Bone oil.

PYROCOPOL *v.* Resins.

PYROCRESOLS $C_{15}H_{14}O$. A group of isomeric bodies, three in number, discovered by Schwarz in coal-tar, and more particularly examined by Bott (S. C. I. 1887, 646).

α-Pyrocresol crystallises in large shining plates, exhibiting a bluish-green fluorescence; readily soluble in benzene, chloroform, carbon tetrachloride, carbon disulphide, &c.; less so in acetic acid, alcohol, and ether; and insoluble in water and alkalis. Soluble also without action in acetyl chloride, phosphorus trichloride, and solution of phosgene gas. M.p. 196°, and readily sublimes.

β-Pyrocresol. Melts at 124°, and crystallises in small needles or laminæ.

γ-Pyrocresol differs from its isomers by its extreme solubility in all solvents; it invariably crystallises in needles, m.p. 104–105°, and does not sublime.

On oxidation by means of chromic acid in acetic acid solution the pyrocresols take up an atom of oxygen and become $C_{15}H_{12}O_2$.

α-Pyrocresol oxide, m.p. 168°, forms yellowish needles; very soluble in acetic acid and alcohol.

β-Pyrocresol oxide, m.p. 95°.

γ-Pyrocresol oxide crystallises in small rhombic plates, which turn red on exposure to light.

α-Tetranitro-pyrocresol oxide $C_{15}H_8(NO_2)_4O_2$, crystallises from nitrobenzene or glacial acetic acid in small yellowish plates, which, on heating, burn with a flash. Is insoluble in caustic potash, and sparingly soluble in alcohol.

β-Tetranitro-pyrocresol oxide resembles the α- compound, but is more soluble in alcohol.

γ-Tetranitro-pyrocresol oxide forms a granular mass of a pale-yellow colour. More soluble in alcohol than the α- compound.

Halogen derivatives have also been prepared. *α-Dibromopyrocresol* $C_{15}H_{12}Br_2O$, is obtained in the form of thick, elongated plates. M.p. 215°.

PYRODINE $C_6H_5.N_2H_2.C_2H_3O$. *Phenylhydrazine acetyl.* A white crystalline powder, very sparingly soluble in cold water, and possessing very little taste.

Is a powerful antipyretic. It reduces fever temperature quickly, and maintains the temperature at a low level for some hours, producing marked perspiration, but not nausea, vomiting, or collapse. It is especially applicable in cases of pneumonia, scarlet fever, and typhus. Given in small doses in the latter disease it enables the patient to pass through the fever at a low temperature range without delaying the crisis, and it seems also to shorten the period of convalescence. It is less applicable in cases of typhoid, owing to the early exhibition of toxic symptoms. Given in often repeated doses at short intervals it easily shows toxic properties, and these depend on the action on the blood, producing hæmoglobinæmia. It should not be given (unless the temperature be very high) oftener than once in 18 or 24 hours, and it is not safe to continue its use for more than a few days. The dose for children is 2–4 grains, for adults 8–12 grains. It is a much more powerful antipyretic than either antipyrine, antifebrine, or phenacetine; but it is also much more toxic than these bodies. This disadvantage is reduced by the fact that it is rarely necessary to give more than one dose in 12 to 18 hours, as the temperature is kept low for a longer period than by any of the other antipyretics. It reduces the pulse as well as the temperature, and often causes diuresis (J. Dreschfeld, S. C. I., 1888, 765), *v.* Phenylhydrazine acetyl.

PYROGALLIC ACID, PYROGALLOL, *v.* Phenol and its homologues.

PYROGUAIACIN *v.* *Guaiacum*, art. Resins.

PYROLIGNATES *v.* Acetic acid.

PYROLIGNEOUS ACID *v.* Acetic acid.

PYROLUSITE *Manganese dioxide v.* Manganese.

PYROMETERS *v.* Fuel; also Thermometer.

PYROPHANITE. A manganese titanate $MnTiO_3$, found by Hamberg embedded in calcite occurring in the neighbourhood of Harstigen. Crystals belong to the rhombohedral-hexagonal system, and are isomorphous with titanic iron ore $FeTiO_3$; brilliant metallic lustre and deep red tint; powder, yellow with slight tinge of green; sp.gr. 4·537.

PYROPHORUS (from the Gk. *πῦρ*, fire; and *φέρω*, I bear) is a word which denotes in its widest sense any substance capable of taking fire spontaneously or on very slight elevation of temperature, as is the case with phosphorus, phosphuretted hydrogen, cacodyl, &c. If iron, cobalt, or nickel be reduced by hydogen from their oxides at a low red heat, the metal is obtained in such a fine state of division as to become incandescent by the oxidising action of the atmosphere; this rapid oxidation is facilitated by the interposition of some infusible material, as alumina or magnesia, between the particles of oxide. When lead tartrate is heated in a glass tube, the lead is left in a very fine state of division, so that if the tube be hermetically sealed, then allowed to cool, the finely-divided particles of lead will, on opening the tube, immediately take fire on coming in contact with the air. The reason of this is that the ratio of the surface exposed, when in a fine state of division, to the mass to be heated is so great that the oxidation of the exposed surface is sufficient to bring the mass to incandescence. The sulphides of potassium, sodium, and lithium, obtained by igniting the corresponding sulphates with lampblack in a covered crucible, are left in a finely-divided state, mixed with charcoal, and burn spontaneously on exposure to air. Homberg's pyrophorus is obtained by heating alum with lampblack, starch, or flour.

PYRORACEMIC ACID *Pyruvic acid* $CH_3.CO.CO_2H$. An acid formed by the distillation of tartaric acid and of cream of tartar; also formed by the distillation of glyceric acid and oxidising lactic acid by means of potassium permanganate. Has been prepared synthetically by the action of hydrochloric acid on acetyl cyanide (Claisen and Shadwell, B. 11, 1,563). Best obtained by heating 1 part tartaric acid with 2 parts of acid potassium sulphate to 220°. A liquid, b.p. 165, and sp.gr. 1·288 $\frac{18^{\circ}}{}$, which tends to polymerise on standing. Combines with nascent hydrogen to form lactic acid. Forms unstable salts, which pass into gummy masses on heating.

PYRORELIN *v.* Resins.

PYROSINE *v.* Triphenylmethane colouring matters.

PYROTECHNY. The art of making fireworks. Although formerly applied to the smelting and roasting of metallic ores, and to other metallurgical processes involving the use of fire, the term 'pyrotechny' has become narrowed down in modern times so as to include only those effects of fire that are produced mainly for scenic displays. That mixtures of certain substances, some of them more or less familiar, when ignited were capable of producing brilliant and startling effects was known to the early ancients. The art of preparing such mixtures, and of manipulating their mode of combustion, had arrived at a considerable degree of perfection long before the true nature of even the commonest of the materials was known, and before the true principles underlying their use were in the least understood. For these reasons it is that the art of pyrotechny, more perhaps than any other art carried on at the present day, is conducted so largely by 'rule of thumb.'

Pyrotechny is said to have had its origin in the East, firework displays being well known in China for many centuries prior to their introduction into Europe, and even to this day the Chinese and Japanese excel in the production of certain fireworks of great beauty. In Europe pyrotechny was first practised by the Florentines, towards the end of the 13th century, at the time that the knowledge of gunpowder began to be diffused among the western peoples; from Italy the art spread to France, and thence to England and Germany.

Notwithstanding the great variety of effects produced by the many different kinds of fireworks, they all have certain fundamental essentials in common. All fireworks contain a combustible substance, and a supporter of combustion. The combustible, or the *fuel*, may be either one or more of a great variety of substances, such as sulphur, carbon, shellac, resin, pitch, starch, sugar, lycopodium, various picrates, particularly the potassium and ammonium salts; various sulphides, as those of iron, antimony, arsenic; various metals, as iron, antimony, zinc, copper, magnesium, &c.

The supporters of combustion are mainly certain oxygen salts, such as chlorates and nitrates, which are readily able to give up their supply of oxygen to the combustible bodies. The pyrotechnist seldom supplies the fuel with a sufficient amount of the oxygen salt to bring about the complete combustion of the former. The object of the firework-maker is not to discharge into the air the completely oxidised products of combustion, but rather to throw out a certain quantity of material which is in a condition to enter into active combination with the oxygen of the air and to carry on its combustion at the expense of this outside supply of oxygen, many of the combustible substances thus emitted being among the products of the complex chemical reactions which are going forward at the time.

The exact nature of the chemical changes which accompany the burning of a firework are little known. The various mixtures, therefore, which are used to produce certain results have, in most cases, been arrived at, not by processes of scientific reasoning, but by purely empirical rules. Although the art of pyrotechny is regarded as a chemical one, it embraces many mechanical considerations and details which are of no less importance to the production of scenic displays than those which are more distinctly chemical.

For convenience the subject may be subdivided as follows:

1. Preparation of mixtures.
2. Manufacture of cases.
3. Loading of cases.
4. Various accessories, as quick-match, touch-paper, leaders, port-fires.

1. The mixtures used in pyrotechny are called compositions or fuses, and their preparation requires some care. In this branch of the work a knowledge of chemistry is of the greatest importance to the pyrotechnist, in order that he may not only get the best results out of his materials, but also that he may avoid the dangers which attend the use of the highly explosive combinations he has to deal with. Many mixtures also are liable to undergo chemical decomposition, so that they can only be employed when the firework is to be used within a short time of its manufacture. Other mixtures are liable to more rapid spontaneous decomposition, resulting in the ignition and explosion of the materials.

In former days most mixtures were more complex, containing more ingredients than those used at the present time; particularly is this the case with mixtures for coloured effects. This is doubtless due chiefly to the greater purity of modern chemicals, for it is well known that a strontium salt, for example, which contains any quantity of a sodium salt with it will have the crimson colour it imparts to a flame more or less completely masked by the yellow of the sodium. In fact, the purity of the substances used is a point of the highest importance.

The staple materials employed in a great number of fuses are potassium nitrate (known as 'petre'), sulphur, charcoal ('coal'), and meal powder ('meal'). The addition of either 'petre' or 'meal' to a fuse has the effect of making it quicker, while the addition of sulphur slackens it; *e.g.* quick-match made from meal, 6 parts; sulphur, 1 part, burns with the greatest violence; while that made from meal, 1 part, and sulphur, 1 part, will scarcely burn at all.

The nitre used is always in the form of meal. The sulphur should be crushed lump in preference to flowers; in either case it must be carefully washed free from acid and dried. Most manufacturers avoid the use of 'chemical charcoal,' as it is termed—*i.e.* charcoal which has been made by distillation in retorts for the manufacture of pyroligneous acid. The weighed materials are thrown upon a table, rolled down with a wooden roller exactly resembling a cook's rolling-pin, and thoroughly mixed by being sifted together through sieves. Every pyrotechnist has his own particular formulæ, which are usually kept more or less as trade secrets; the variety of mixtures which are used for the same firework will be seen from the following instances:—

Rockets.

Sulphur	8	1	1	2	4	2	4	8	4	12	1	1
Charcoal	27	2	2	12	8	4	7	11	5	17	2	4
Nitre	36	4	4	20	16	9	16	32	16	50	5	8
Meal powder	6	2	1	1	3	—	—	—	—	—	—	—

Roman candles.

Sulphur	1	2	2	3	3	4	4	7
Charcoal	2	3	3	3	1	1	3	8
Nitre	4	2	9	8	4	5	8	21
Meal powder	3	8	4	3	5	4	8	12

Tourbillons.

Sulphur	1	3	3	7	3	4	4	2	4
Nitre	4	16	5	10	8	17	17	4	8
Charcoal	2	8	3	4	3	4	5	—	—
Meal powder	1	8	11	24	16	—	—	4	9
Steel filings	—	—	—	8	6	—	—	—	—
Cast-iron borings	—	—	—		—	6	8	3	4

It is in the preparation of mixtures for colour effects that the purity of the chemicals is of the greatest importance. Coloured stars for shells, Roman candles, rockets, &c., consist of small compacted masses of composition; they are called 'cut' or 'naked' stars, and 'pill-box' stars, according to the method of their manufacture. 'Naked' stars are made by moistening the composition with a solution of either gum, shellac, or with starch, spreading it out upon a slab with a spatula, and marking the surface by cross parallel lines into small squares. When nearly dry, it is broken up by the marks, and exposed until dry. The rough edges obtained by this method enable the star to ignite readily. Stars made this way must contain nitre as the oxygen supply, and not potassium chlorate; for although chlorate mixtures burn more fiercely, they are more difficult to ignite.

The following formulæ are for constructing 'naked' stars, known as 'comet' or 'tailed' stars:—

Sulphur . .	5	24	2	—	1	2
Nitre . .	5	24	9	—	10	20
Charcoal . .	2	8	2	3	6	12
Vegetable black.	1	3	3	6	—	—
Meal powder .	8	30	6	16	5	7

'Pill-box' stars are made by compressing the dry composition into short cylinders of paper, and inclosing a piece of quick-match for their ignition. These all contain chlorates, as will be seen by the following formulæ:—

—	Blue stars with sugar					Blue stars without sugar					
Potassium chlorate . .	8	36	40	6	40	5	40	6	8	2	5
Calomel	4	18	24	5	—	4	20	2	2	—	—
Sugar	5	12	12	4	9	—	—	—	—	—	—
Copper sulphide . . .	3	22	12	—	22	4	20	—	2	—	1
Stearin	—	1	1	—	2	—	—	—	—	—	—
Oxychloride of copper .	—	—	3	—	—	—	2	—	—	1	1
Ammonium chloride . .	—	—	—	—	6	-	—	—	—	—	—
Copper filings . . .	—	—	—	1	—	—	—	—	—	—	—
Shellac	—	—	—	—	—	1	5	—	—	—	—
Sulphur	—	—	—	—	—	—	—	3	4	1	2
Copper oxide . . .	—	—	—	—	—	—	—	1	1	—	—

The use of copper chlorate is practically inadmissible, on account of its deliquescence, as well as its danger. The well-known substitute (obtained by dissolving copper sulphate and potassium chlorate together in water, evaporating to dryness, moistening with ammonia and again drying), called Chertier's copper, although yielding excellent blues, is practically abandoned by manufacturers on account of its liability to explode.

The following formulæ may be used for red, green, and yellow stars:—

—	Red				Green					Yellow			
Potassium chlorate . . .	16	8	16	28	16	8	1	—	6	8	4	12	4
Sulphur	5	6	—	—	5	7	1	1	—	—	—	—	1
Charcoal.	1	1	—	—	1	1	—	—	—	—	—	—	—
Calomel	—	—	—	12	—	—	—	—	5	—	—	—	—
Shellac	—	1	—	—	—	2	—	—	—	2	1	3	—
Sugar	—	—	7	12	—	—	—	—	5	—	—	—	—
Strontium nitrate . . .	16	16	—	—	—	—	—	—	—	—	—	—	—
Strontium carbonate . .	—	—	11	5	—	—	—	—	—	—	—	—	—
Barium nitrate . . .	—	—	—	—	16	21	—	—	7	—	—	—	—
Barium chlorate . . .	—	—	—	—	—	3	2	4	3	—	—	—	—
Sodium oxalate . . .	—	—	—	—	—	—	—	—	—	3	2	8	1

Coloured mixtures are sometimes made up with magnesium filings, to produce specially brilliant stars and asteroids. These vary only slightly from the above formulæ, with the addition of magnesium filings; one illustration of each for red, green, blue, yellow, and white may be quoted.

—	Red	Green	Blue	Yellow	White
Potassium chlorate	2	—	5	4	—
Sulphur	2	1	2	—	4
Charcoal	1	—	—	—	—
Shellac	—	3	1	1	—
Calomel	—	—	2	—	—
Magnesium filings	2	2	2	1	2
Strontium nitrate	8	—	—	—	—
Barium chlorate	—	12	—	—	—
Copper oxychloride . . .	—	—	2	—	—
Sodium oxalate	—	—	—	2	—
Potassium nitrate	—	—	—	—	12
Antimony sulphide . . .	—	—	—	—	1

2. *The manufacture of cases.*—All cases are made of paper, and the selection of the paper is a point of some importance. The paper varies in quality and stoutness, according to the particular kind of firework to be made and to the amount of strain which will be put upon the case. In some instances the material of the paper influences the character of the display produced by a particular firework. For example, the Japanese 'spur fire,' which on burning throws scintillations of a peculiar beauty, owes this quality partly to the special paper of which the case is made, for if the same mixture be introduced into a case made of another paper it will be found to have lost to a large extent the property of throwing out these characteristic scintillations. Most of the papers used are of a superior quality, as it is found that greater strength can be obtained by the use of a smaller quantity of a good paper than by employing more of one of inferior quality; paper which is 'loaded' or adulterated cannot be used. The majority of cases are made of brown paper, although some, and more especially the smaller sorts, as crackers, Catherine wheels, &c., are always made of white cartridge. In a large factory several scores of different papers will be used. The paper is cut to the various sizes required by cutting machinery, and into certain special irregular shapes by dies.

Owing to the great variety in size required, the cases are all made by hand, and, but for slight variations, in the same manner. The tools employed are of the very simplest description, consisting of a wooden or metal roller called the 'former,' and a short wooden board with a handle on one side, known as the 'rolling board.' For the larger cases the paper is pasted over its whole surface, and rolled round the 'former,' the operation being done on a narrow slate table. The rolling board is then passed rapidly over it a few times with a firm steady pressure (fig. 1).

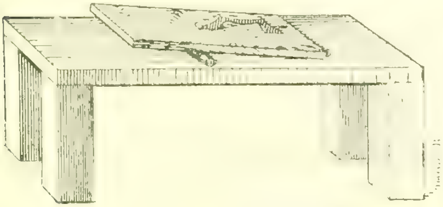


FIG. 1.

The former is then withdrawn, and the case stood on end until it is so far dry that it can be laid on its side without risk of its losing its cylindrical shape. They are then stacked in bins in a chamber through which a current of warm air is circulating, in order to render them perfectly dry. In many fireworks the cases have to be partially closed, or constricted near to one end. This is technically known as 'choking.' It may be effected in two ways, either by compressing the walls of the case to the desired extent, or by partially filling the mouth of the case with clay. When the first of these plans is adopted, the operation is performed when the case is freshly made, and only partially dry. For small fireworks it is done by means of a hand lever, made of two blades of steel, and screwed to the edge of the table (fig. 2).

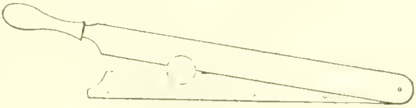


FIG. 2.

For larger cases a foot lever is employed. A noose of cord is looped round the case, one end being fastened to a hook in a wall, or upright post, while the other passes over a wheel to a lever upon the floor, which can be worked by the foot. As the cases have to be choked down to a certain definite orifice, a 'choking-pin' (fig. 3) is inserted at the time the constriction is being made, which also secures another essential condition, viz. that the choke shall be central. The case is tied round the choke with a string suitable in thickness to the size case, and the whole is then allowed to dry.

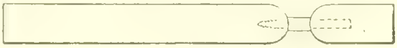


FIG. 3.

When the constriction is effected by means of a clay plug, the operation is performed at the time of loading.

For small cases the paper is pasted only along the edges; the former, in this instance a thick metal wire, is placed nearly in the middle of the paper. One end is then folded over nearly to the other, and the double paper rolled over the former (fig. 4).

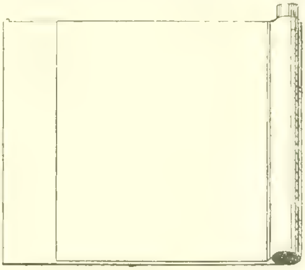


FIG. 4.

The case may be closed at one end by folding the paper in upon the end of the former. These cases require no special drying. Light cases, such as these, are usually made by women, one operator being able to turn out many hundreds in an hour.

Besides cylindrical cases, there are cases made in the form of a sphere, known as 'shells.' These shells, which are constructed of various sizes, up to even 24 inches in diameter, are made by a process technically known as the 'wet-broke' process. Brown paper of a specially good quality is thoroughly pasted on both sides; strips are then *torn* from the pasted length, and laid upon the inside of a hemispherical bowl or mould, the strips radiating upwards from the centre to the circumference, the ends lapping over the edge of the mould; the workman continues this process until the desired thickness of paper is obtained, which will vary according to the size of the shell from about ⅓ to 1 inch. It is then removed from the mould and allowed to dry, when it presents the appearance shown in fig. 5. These hemispheres are then placed in a lathe, and the ragged lips or rims carefully turned off. A good workman will so turn out these paper hemispheres, that the cut edge shows a most beautiful and perfectly homogeneous section. Two of these hemispheres are securely glued together to form the complete shell. These shells are destined to carry coloured stars, and to be fired from a mortar; the mould in which they are made has therefore a slightly raised ridge running part of the way down from the circumference, which produces a corresponding indentation, or 'dimple' in the shell, which allows of room between the shell and the side of the mortar for communicating the fire to the propelling charge below.

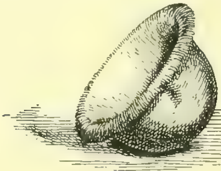


Fig. 5.

3. *Loading the cases.*—This operation varies in details according to the special firework to be filled, but, broadly speaking, it may be divided into two sections, viz. *loose-filling* and *ramming.* The apparatus employed in the first of these methods is a metal funnel, of an elongated shape, and a wire, the operation being known as 'wire and funnel' filling. The wire is usually square, and of such a thickness that it will just pass through the end of the funnel. The case to be filled, if a choked case, is placed upon a stand with its choked end fitted upon a nipple fixed for its reception; the nose of the funnel is then inserted into the open end of the case, and by drawing the wire quickly up and down the composition is driven uniformly into the case. When full to the required height, usually determined by a mark upon the wire, the case is closed up. With small fireworks (such as squibs &c.) this is done by firmly squeezing the end of the case with a tool known as the 'closing-in' machine, and finally dipping the end into a composition, usually red in colour, and technically called 'dip.'

Glue and red-lead is the most common mixture for 'dip.'

Long narrow cases (such as are used for crackers and Catherine wheels) are filled without the use of a stand. For the last-named of these fireworks no special tools are required, the long narrow tube being wound by hand upon a small wooden disk, and secured by strips of tape or paper glued across. In the manufacture of crackers two special pieces of apparatus are employed. The first is a rolling or flatting machine. The filled cases are passed between the rollers of this tool, and thereby squeezed flat, the pressure being carefully regulated to the required degree. The other tool is the bending machine. It consists of two upright rectangular brass pillars fastened to a base at such a distance apart as to allow of four of the flattened cases to lie abreast between them (fig. 6). The cases are bent backward and forward over steel wires about the thickness of a stout steel knitting-needle, until the requisite number of bends is obtained; they are then pressed firmly down with a piece of wood, and removed from the machine. The wires drop out, and are ready for the next set of cases.

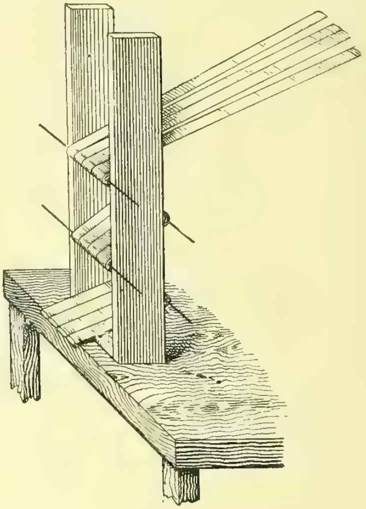


Fig. 6.

The bent cases are then tied up into the familiar compact form with a suitable thread, and the ends primed in the usual way with touch-paper.

Of the second method of loading cases, in which the composition is rammed in, two illustrations may be given, viz. the Roman candle, in which the mixture is gently rammed, and the rocket, in which it is 'malleted.' The case for a Roman candle is a straight or unchoked one. It is placed upon a block, called a 'settle,' the projecting core A of which (fig. 7) exactly fits into the case.

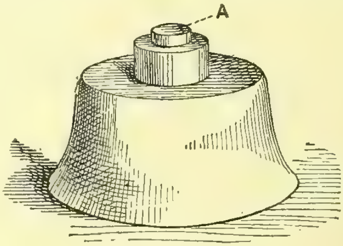


Fig. 7.

A small quantity of finely-powdered and sifted clay is first introduced, and tightly driven lown by means of the 'rammer,' a wooden rod, vhich loosely fits into the case. A few smart blows from a mallet upon the head of the ammer will compress the clay into a solid mass, vhich should occupy about ½ an inch up the ase. Fine potters' clay is usually recommended, out London pyrotechnists use the common London lay. The use of plaster of Paris instead of clay ias been introduced by the Americans, and is said to be much superior. The plaster is mixed vith a little water until of about the consistency of soft putty; a pellet is moulded with the ingers, dropped into the case, and gently pressed oy the rammer. The case is next to be filled vith composition, and coloured stars, alternaing. Each layer of mixture is introduced in two juantities, and rammed down by simply 'jumpng' the rammer. If more force is applied the stars are liable to be crushed. Care is taken to egulate the charge of mixture, so that each star shall, as far as possible, be blown out to the same listance. Various devices are adopted to secure he ignition of the star, to prevent it becoming a blind star' as it is termed, one being to make he stars with a hole in them, which is primed vith a piece of quick-match.

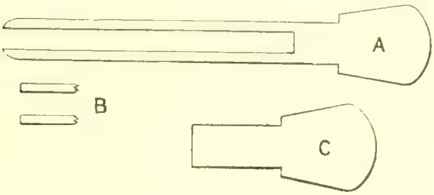


FIG. 8.

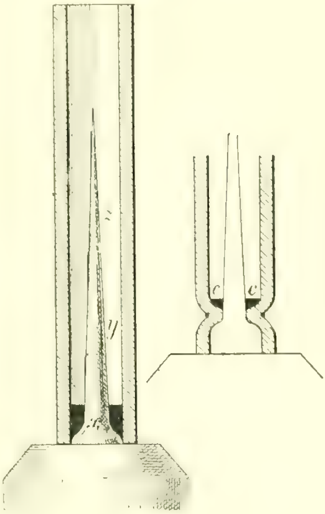


FIG. 9.

Rockets are loaded by the mixture being orcibly rammed into the case by a mallet, and is this firework is in some respect of a special onstruction, in which the exact relation of all the oarts to one another has to be made with much iicety, its construction may be described at reater length. The rocket is a hollow firework, ind therefore has to be constructed with special ools. (Very small rockets are often packed solid, ind a hole bored up the inside with a common lrill.) These consist of a steel conical spindle, or ore, firmly screwed into a base of either hard vood or brass, the length and thickness of this spindle varying for each size rocket, a set of vooden rammers, or drifts,' of different lengths, ind having a cylindrical hole bored nearly up to he head. The number of drifts required for ach rocket depends also upon the size; for arger cases four are used. Formerly a 'mould' vas employed; this was a strong wooden jacket, o surround the case during the loading operaion, to prevent it from splitting; but this is iever employed by the manufacturer to-day, owing to improvements in the case-making, resulting partly from the use of better paper. The ase to be charged is placed upon the spindle, vhich must be stood upon a massive wooden or stone block to prevent vibration. It would be quite impossible, for instance, to load a rocket ightly if hammered on a wooden table or floor. If the case has been previously choked by constriction a rammer with a rounded end, A (fig. 8), and technically called the 'setting-down piece,' is introduced, and driven down with a few sharp taps with a mallet: this is to smooth out any wrinkles in the choked end. To prevent the choke from becoming enlarged by being burnt away a small quantity of clay is introduced, and well 'malleted' in with the longest drift *c* (fig. 9). Except in the case of the largest rockets, most manufacturers prefer to use a straight case, and choke it at the time of loading by ramming in a layer of clay, straight cases being easier and cheaper to make than choked ones; with large rockets, however, there is some risk of the clay choke being blown out. Fig. 9, drawn to scale, shows such a case, with the clay choke and spindle. The composition is introduced into the case in 12 equal quantities, measured by a scoop made to hold the exact amount. Each scoopful is malleted well in, the workman being careful to give the same number of blows—usually 18 to 20—and of as nearly equal force as he can judge. As the load rises in the case a shorter 'drift,' with a smaller bore is used. The longest drift, which must be bored large enough to admit the spindle at x, will be 8 times the diameter of the case, exclusive of its head. When the composition reaches one-third up the spindle y (fig. 9), which is known by a mark on the drift, the second drift is brought into use; the ramming is continued with No. 2 until the load reaches z (fig. 9), again ascertained by a mark on the second drift. The third drift loads up to the top of the spindle, when the hollow drifts are replaced by a solid one, C (fig. 8). The drifts diminish in length by 2 diameters of the case, the three hollow ones being respectively 8, 6, 4, while the solid one is 2 diameters, the 'setting-down' piece being the same length as the longest drift, but with a round end. The case is filled to within about 1 diameter of the top, and then a layer of clay is driven down. The case is removed from the spindle by a gentle twist or turn in one direction only. The nomenclature adopted by the manufacturers to denote various sizes in rockets is the old-fashioned and arbitrary one of 'pounds' and 'ounces'—these weights referring not to the weight of the rocket, but to the weight of a leaden ball of the same diameter as the mould formerly used for loading. As every maker varies in the thickness of his cases, this conveys no exact criterion of the real size of the rocket. By general consent, a case of $1\frac{1}{8}$-inch bore is called a 'pound' rocket, and a $\frac{1}{2}$-inch case an 'ounce' rocket. The following table gives, in a convenient form, the exact sizes of the various parts. The inside diameter is given in eighths of inches, and the relation which should subsist between this measurement and that of thickness of the case, length, and thickness of the stick, will be seen at a glance :—

Inside diameter in eighths	Outside diameter	Length of case in inches	Length of spindle	Diameter of bottom of spindle	Length of stick in inches	Thickness of stick
$\frac{3}{8}$	$\frac{4\frac{1}{2}}{8}$	3	$2\frac{1}{4}$	$\frac{3}{20}$	$3 \times 8 = 24$	$\frac{1\frac{1}{2}}{8} \times \frac{1\frac{1}{2}}{8}$
$\frac{4}{8}$	$\frac{6}{8}$	4	3	$\frac{4}{20}$	$4 \times 8 = 32$	$\frac{2}{8} \times \frac{2}{8}$
$\frac{5}{8}$	$\frac{7\frac{1}{2}}{8}$	5	$3\frac{3}{4}$	$\frac{5}{20}$	$5 \times 8 = 40$	$\frac{2\frac{1}{2}}{8} \times \frac{2\frac{1}{2}}{8}$
$\frac{6}{8}$	$\frac{9}{8}$	6	$4\frac{1}{2}$	$\frac{6}{20}$	$6 \times 8 = 48$	$\frac{3}{8} \times \frac{3}{8}$
$\frac{7}{8}$	$\frac{10\frac{1}{2}}{8}$	7	$5\frac{1}{4}$	$\frac{7}{20}$	$7 \times 8 = 56$	$\frac{3\frac{1}{2}}{8} \times \frac{3\frac{1}{2}}{8}$
$\frac{8}{8}$	$\frac{12}{8}$	8	6	$\frac{8}{20}$	$8 \times 8 = 64$	$\frac{4}{8} \times \frac{4}{8}$
$\frac{9}{8}$	$\frac{13\frac{1}{2}}{8}$	9	$6\frac{3}{4}$	$\frac{9}{20}$	$9 \times 8 = 72$	$\frac{4\frac{1}{2}}{8} \times \frac{4\frac{1}{2}}{8}$
$\frac{10}{8}$	$\frac{15}{8}$	10	$7\frac{1}{2}$	$\frac{10}{20}$	$10 \times 8 = 80$	$\frac{5}{8} \times \frac{5}{8}$

The stick may be attached to the rocket by being securely tied with string near to the two ends of the case. Modern manufacturers usually bind upon the rocket case a smaller case, just large enough to admit the end of the stick when it has been roughly rounded. Two short spikes are driven into this rounded part of the stick, which, on being thrust up into the case and twisted, cause it to hold very securely. A rocket when laid across the finger should just balance when the point of support is about an inch along the stick, away from the mouth of the case.

The weight of composition required to load a rocket may be found by the following formula, where d = internal diameter of case in eighths of inches :—

$$\frac{d^3}{9} = \text{number of drachms.}$$

e.g. the charge for a $\frac{9}{8}$ (so-called 'pound' rocket) =

$$\frac{9^3}{9} = 81 \text{ drachms} = 5 \text{ ozs. } 1 \text{ dr.}$$

Rockets are always made to carry up a load of various combustibles ; these are contained in a slight paper case, known as the 'pot,' which is glued to the head of the rocket. This pot is to be burst, and its ignited contents thrown out, at the moment the rocket reaches the top of its flight, and before it has turned over. The bursting of the pot, and the inflammation of its contents are secured by a small quantity of powder, known as 'bursting powder,' the weight of which is usually about $\frac{1}{9}$ the weight of the materials in the pot. This 'garniture' of a rocket may consist of a variety of things, such as gold or silver rain, coloured stars, magnesium stars, parachutes, whistling fireworks, &c.

Rockets garnished with parachutes are called 'asteroid rockets.' The parachute is made of thin alpaca, silk, or tissue paper. The latter has to be strengthened by a thread of cotton round its edge, and the paper thoroughly softened by a process of crumpling, to insure the parachute opening when thrown out. Suspended by threads from the parachute is the case, loaded with coloured compositions, usually layers of different mixtures, so that the colour may change as the parachute sails along.

The whistling firework consists of a short paper case, closed at one end, and charged with a composition consisting of picrate of potash 3 parts and nitre 2 parts, or the picrate 15 parts mixed with asphaltum 1 part. The case is not choked, nor is the mouth shaped; but on ignition the outrushing flames and gas emit a shrill weird whistling sound, gradually rising in a 'crescendo' to a maximum loudness and then falling with a rapid diminuendo. Usually five of these are loaded into a 'pot' to garnish a rocket.

The weight of the load which a rocket can safely be made to carry is the same as that of the composition with which it is filled; thus a $\frac{9}{8}$ ('pound') rocket can be made to carry up a load of 5 ozs. 1 dr.

Of all the materials which can be used to garnish rockets, that which produces by far the most brilliant effect for the weight and cost is phosphorus ; but the extreme danger attending the manipulation of this substance has prevented its use by pyrotechnists to any extent. Patents have been taken from time to time with a view to diminish or overcome this difficulty. One of these consists in packing the phosphorus, cut in short sticks of about 1 inch, into a perforated paper cage, which has been previously dipped in melted paraffin wax. The cage, with its load, is immersed in a tin can of water until required. When the rocket is ready to be fired, one of these paper cages is taken, the excess of water drained off, and the cage introduced into the rocket pot, into which it just fits. On the bottom of the pot a layer of bursting powder has previously been placed, and covered over with a thin piece of waterproofed paper.

When the phosphorus is introduced the cone is fitted in and the rocket fired.

4. *Touch-paper* is made by impregnating a thin paper—by general consent, blue—with potassium nitrate. The paper commonly employed is 12-lb. double crown. The sheets are spread out and brushed over on one side only with a solution of nitre, containing 1 oz. of the salt to a pint of water. The paper is used for enveloping the live end of fireworks.

Slow-match is prepared by soaking blotting paper in a solution of lead nitrate. Blotting paper is brushed on both sides with a solution containing $2\frac{1}{2}$ ozs. of the nitrate to a pint of water. When dry six layers of the paper are pasted together and pressed flat, forming, when again dried, a stiff board. This is then cut into suitable strips with a sharp knife.

Quick-match is made by impregnating cotton with a mixture of starch paste and meal powder. Meal powder is stirred into hot thin starch paste until it has the consistency of paint and is quite smooth. Lamp cotton, with six or eight strands, is then coiled into the vessel containing the 'meal paste,' the cotton being pressed carefully down with a wooden stick to insure its being thoroughly soaked. It is then wound out on to wooden frames, usually about 6 feet high and $2\frac{1}{2}$ feet wide; these frames are provided with pivots, so that they can be swung upon a support. The frame is turned slowly over and over by one workman, while a second feeds out the cotton through his hand, rounding the wet thread with his fingers as it passes. The frame is then laid down and meal powder sifted first on one side and then on the other; the cotton is then allowed to dry. When cut it ought to show a perfectly black section. It is preserved in long boxes, as it is necessary to guard it from getting cracked.

Leaders consist of thin paper tubes, through which quick-match is threaded, in order to convey fire rapidly from one firework to another. The tubes have to be such a size as to allow the match to be introduced without any forcible pushing. The more closely the match fits the pipe the more rapidly does the combustion propagate itself through the length. The pipes are made to any length by slightly pinching the end of one piece and pushing it into the next, the join being bound over with a slip of pasted paper. They can be made to take various angles by cutting away the paper at the elbow of the bend.

Port-fires consist of cases about 10 or 12 inches long, made very thin, usually three or four turns of paper only, and $\frac{3}{8}$ or $\frac{1}{4}$-inch bore, filled with a slow burning mixture—such as nitre 6 parts, sulphur 2, meal powder 1.

One or two technical applications of pyrotechny other than the manufacture of fireworks for spectacular display may be briefly mentioned.

The so-called 'drain rocket' is specially made to emit large volumes of smoke, and often a powerful stench, and is used to detect leaks and stoppages in drains. In so far as it does not travel, but is stationary, the term rocket as applied to it is a misnomer. The 'trawler's flare' is a useful firework to enable fishermen to see the floats and buoys of their nets by night. It consists of a case about 4 inches long and 1 inch diameter, filled with a flaring mixture, and attached to a wooden handle. An ingenious device is adopted to enable the men to light them in wind and rain. When the cases are loaded a small quantity of a chlorate of potash mixture is spread on the end; this is then papered over, a strip of tape being laid under the paper and its end left projecting as a little 'tab' against the side of the case. The handle is bored out, and into the hole fits a little wooden stopper or plug, the tip of which has been coated with red phosphorus. To ignite the flare the sailor pulls the tab and peels off the paper covering, and rubs the end of the wooden stopper across the mouth of the firework, when the mixture is inflamed.

A modified form of rocket is used as a means of carrying a thin line to ships in distress round the coast, forming a part of what is known as the 'rocket apparatus.' These rockets are a combination of two rockets in one case, one being a continuation of the other, so that when the discharge of the first compartment has carried the instrument to its full height the second is ignited and gives it an additional impetus, thereby greatly increasing its range.

G. S. N.

PYROXYLIC SPIRIT (*crude Methyl alcohol*) *v.* METHYL ALCOHOL.

PYROXYLINE *v.* PHOTOGRAPHY.

PYRRHOTINE (*Ferrous sulphide*) *v.* IRON.

PYRROL *v.* BONE OIL.

PYRROLINE *v.* BONE OIL.

Q

QUARTATION *v.* ASSAYING.

QUARTZ. An old German mining term, now used as a generic name for all the native forms of crystallised and crypto-crystalline silica, excepting the rare minerals, tridymite, asmanite, and lussatite. Quartz crystallises in the hexagonal system. For details of its crystallisation (a complex subject of no technological interest), *v.* G. Rose, Abh. Ber. Ak. 1846; Des Cloiseaux's Mémoire, 1855; and E. Weiss, Abh. Nat. Ges. Halle, 5, 1860, 53. The cleavage of quartz is rhombohedral, but usually imperfect, the mineral generally showing a conchoidal fracture. The hardness (7), sp.gr. (mean 2·65), and vitreous lustre are useful aids in distinguishing quartz from other minerals. It is practically insoluble in acids, except hydrofluoric, and infusible, except before the oxyhydrogen blowpipe. C. V. Boys has obtained fibres of quartz of excessive tenuity by rapidly drawing out the fused mineral by means of an attached arrow, shot into the air from a trigger-bow. Such fibres, being strong and elastic, may be advantageously used as torsion-fibres in delicate physical experiments (P. M. [5] 23, 1887, 489). Boys has also shown that quartz, especially after fusion, is a valuable insulator of electricity, even in moist air (P. M. [5] 28, 1889, 14).

Many varieties of quartz are cut and polished for use as ornamental stones. Transparent and colourless quartz, termed *Rock-crystal*, is often known locally as 'diamond,' but even when judiciously cut it lacks lustre. 'Carrara diamonds' are beautiful limpid crystals, found in cavities in Carrara marble; but most rock-crystal occurs in granite, gneiss, and other siliceous rocks. On the disintegration of such rocks the crystal is set free, and, being washed into streams, may ultimately form rolled pebbles. The 'pebbles' for spectacle-lenses are mostly obtained from Brazil and Madagascar. They should be cut at right angles to the axis of the prism, to avoid double refraction. Lenses of crystal are readily distinguished from those of glass when placed between crossed tourmalines in the polarising-pincers. In the Cinque Cento period rock-crystal was largely employed for ornamental carvings, and it is still highly prized for this purpose in China. Spheres of rock-crystal, often exhibiting marked double refraction, are cut in Japan, and, of late years, have been worked in Germany. By some of the Indians of North America crystal was formerly used for arrow-heads. Rock-crystal not unfrequently contains cavities with liquid, or is penetrated by acicular crystals of actinolite, schorl, and other minerals. Crystal traversed by needles of rutile, is generally known to jewellers as 'Cupid's arrows' or 'Venus's hair.' In *rainbow quartz* iridescent effects are produced by the interference of light reflected from the walls of minute fissures. The chatoyant effect of common *cat's-eye* is due to parallel fibres of an asbestiform mineral traversing the quartz (*v.* CROCIDOLITE). Quartz cat's-eye is obtained from Ceylon, and from Hof in Bavaria. Dull green quartz, inclosing actinolite, is called *prase.*

Rock-crystal frequently assumes a brown tint, and is then known as *smoky quartz,* or *smoky topaz.* The colour has been referred to the presence of a volatile carbonaceous substance, since the crystal, on exposure to moderate heat, becomes yellow. Fine specimens of smoky quartz occur at Pike's Peak, Colorado; in Siberia, and in Madagascar; but the largest have been found in Switzerland. A great number of gigantic crystals were discovered in 1868 on the Tiefengletscher, in Canton Uri. When the colour is very dark, the crystal appears black by reflected light, and is then termed *morion.*

Yellow crystal, sometimes called *citrine,* is known popularly as 'topaz'; hence we hear of 'Scotch topaz,' 'Spanish topaz,' &c. (*v.* CAIRNGORM). Red and yellow quartz, more or less opaque by the mechanical inclosure of ferric oxide or the hydrate, is termed by German mineralogists, *Eisenkiesel.* The *rose-quartz,* found in Bavaria and in Finland, becomes pale on exposure, and is not often cut as an ornamental stone. The *sapphire quartz,* of Golling, in Salzburg, contains inclosures of blue crocidolite. *Aventurine* is quartz with golden spangles, due to flakes of mica or scales of iron oxide. The ordinary brown aventurine is obtained chiefly from Spain and Siberia, but a rare green variety was brought by Colonel Seton Guthrie from Madras. Much of the common so-called aventurine is simply a reddish-brown spangled glass from Venice, easily detected by its inferior hardness.

Amethyst is a term formerly restricted to the purple or violet varieties of quartz, valued in jewellery, since they are the only gem-stones worn in mourning. At about 250°C. most amethysts become yellow. The finest specimens occur in Brazil, Siberia, and India, and in the interior of the agate geodes of Uruguay. At Amethyst Mountain, in the Yellowstone National Park, the mineral is found lining cavities in silicified wood. Amethyst commonly occurs as an aggregate of crystals, the pyramidal summits only being free, while the united prisms, known to lapidaries as 'root of amethyst,' exhibit on fracture a characteristic rippled appearance. Brewster applied the term 'amethyst' to all quartz with this wrinkled fracture. Optical examination reveals the composite character, suggested by the irregular distribution of colour, showing that the mineral is built up of laminæ, with alternate right- and left-handed polarisation. All quartz showing this structure, whatever its colour, is now usually termed amethyst.

Under the name of *chalcedony* are comprised various quartzose minerals, which appear to be aggregates of crypto-crystalline and colloidal silica, the latter being removable by solution of caustic potash (*v.* FLINT). Typical chalcedony is a translucent mineral, with a waxy lustre and fibrous structure, usually occurring in mammillated, botryoidal, and stalactitic forms, lining agate geodes and hollow flints. Many of the coloured varieties are largely used as ring-stones and for engraved seals. Common chalcedony is generally of bluish-grey colour; the red varieties are known as *carnelian* and the brown as *sard* (*v.* AGATE). *Chrysoprase,* found chiefly at Kasemütz, in Silesia, is a bright-green chalcedony, coloured by nickel oxide, and formerly used largely in jewellery, especially when set with diamonds. *Plasma* is a dull-green chalcedony, while *heliotrope,* or 'bloodstone,' is a similar mineral with spots and veins of vivid red colour.

Another group of quartzose minerals is formed by the *jaspers,* comprising all the coloured opaque varieties which present a compact texture (*v.* JASPER). F. W. R.

QUASSIA (*Bitter-wood, Bois de Quassia,* Fr.; *Quassiaholz,* Ger.). The wood of *Picræna excelsa* (Lindley), a large ash-like tree inhabiting the plains and lower mountain slopes of Jamaica and neighbouring islands (*v.* Bentl. a. T. 57). Formerly the quassia of commerce was derived from the allied South American tree *Quassia amara* (Linn.), and the wood of this tree is still employed on the Continent. *Picrasma quassiodes* (Benn) and *Samadera indica* (Gärtn.) also furnish a very similar wood (Ph. [3] 2, 644 a. 654; 20, 41). The intensely bitter taste of the wood of *P. excelsa* is due to the presence of about 0·03 p.c. of a neutral crystalline substance, *quassin.* Compounds possessing similar properties have been isolated from the other trees mentioned; indeed it was from *Q. amara* that quassin was first isolated by Winckler (R. P. 54, 85; 65, 74). It was analysed and further studied by Wiggers, who obtained it from an aqueous infusion of the wood, after separation of pectinous constituents by means of lime or lead carbonate, by evaporation to dryness and extraction with alcohol. The alcoholic solution yielded a crude quassin, which, after purification, assumed the form of white opaque prisms. Dissolved in water, quassin thus obtained gives no precipitate with chlorine, iodine, mercuric chloride, or salts of lead or iron, but forms an insoluble compound with tannin (A. 21, 40).

Improved methods for the preparation of quassin were proposed by Christensen (Ar. Ph. [3] 20, 481), and by Adrian and Moreaux (Rép. de Pharm. 11, 246). Christensen prepares an insoluble tannate directly from a neutralised aqueous infusion of the wood, and this, decomposed by lime or lead carbonate, yields a crude quassin to alcohol. Adrian and Moreaux take advantage of the easy solubility of quassin in alkalis, and extract the wood with water containing alkaline carbonate. The infusion is evaporated and treated with alcohol, when a solution is obtained which, after several processes of purification, yields quassin in crystals.

According to Oliveri and Denaro (G. 14, 1; 15, 6), who employ for its preparation a modified form of Christensen's method, quassin consists of slender colourless iridescent needles, which melt at 210–211°. It has the formula $C_{32}H_{42}O_{10}$. It is very soluble in alcohol, chloroform, and acetic acid, but nearly insoluble in ether. 100 parts of water at 22° dissolve 0·253 parts of quassin. Heated with hydrochloric acid in a closed tube, it yields two molecules of methylchloride and *quassic acid* $C_{30}H_{38}O_{10},H_2O$, a compound melting at 245° and crystallising in silky needles. Oliveri and Denaro are thus led to regard quassin as a dimethyl ether of quassic acid, $C_{28}H_{36}O_6(COOCH_3)_2$. The composition of the metallic salts of quassic acid also shows that it is dibasic. Oliveri (G. 17, 570), by acting on the acid with hydroxylamine hydrochloride, obtains a *dioxime*, $C_{28}H_{38}O_8(C:NOH)_2$, in yellow prisms which melt at 228–230°. The existence of this compound indicates that quassic acid contains two ketonic CO groups. That this is also the case with its dimethyl derivative, quassin, is further shown by Oliveri (G. 18, 169) by the formation of a *phenylhydrazine compound*, $C_{30}H_{42}O_8(CN.NHC_6H_5)_2$, by the action of that reagent on quassin.

Quassin reduces Fehling's solution, but when it is heated with dilute sulphuric acid no glucose is formed. By this treatment it loses a molecule of water, forming an anhydride, *quasside*, $C_{32}H_{40}O_9$. This compound, which is white, amorphous, and bitter, melts at 192–194°, and when boiled with dilute alcohol, takes up again a molecule of water, quassin being re-formed. Quassin may also be converted into the anhydride by heating with acetic anhydride, or even by heat alone at 150° in a current of dry air. If bromine be present *tribromoquasside*, $C_{32}H_{37}Br_3O_9$, results. If quassin be heated with acetic anhydride in presence of sodium acetate the dehydration goes further. In this case two molecules of water are removed, and a *second anhydride*, $C_{32}H_{38}O_8$, a white, pearl-like, amorphous mass, melting at 150–158°, is obtained. Bromine forms with quassin a substitution derivative melting at 155°, *bromoquassin*, $C_{32}H_{41}Br_3O_9$ (?), and phosphorus pentachloride yields *pentachloroquassin*, $C_{32}H_{39}Cl_5O_9$ (?), a yellow powder melting at 119°. A *nitro- derivative* melting at 130° also exists (D. and O.). When quassin is heated with concentrated hydriodic acid and amorphous phosphorus it yields, among other products, *isodurene*, $C_{10}H_{14}$, and a *hydrocarbon*, $C_{14}H_{16}$, which boils at 220–240° (Oliveri, G. 17, 575).

From the recent investigations of Massute (Ar. Ph. [3] 28, 147) it would appear that the bitter crystalline constituents of the different trees mentioned at the beginning of this article, though similar, are not identical. By an improved process this observer obtains from the wood of *Q. amara* four bitter crystalline *quassins*, one of which corresponds with the quassin of Oliveri and Denaro. The others are probably methyl derivatives of this with higher melting-points. From *P. excelsa* the same chemist obtains two crystalline compounds which are designated *picrasmins*. They differ in composition from the *quassins*, but appear also to be methyl derivatives or homologues. One of them yields, by the action of hydrochloric acid, *picrasmic acid*, homologous with the quassic acid of Oliveri and Denaro.

Quassia is sometimes used as a substitute for hops in beer. For methods of its detection see Dragendorff (C. C. 1881, 285 and 299). Allen (An. 1887, 107). A. S.

QUASSIC ACID, QUASSIDE, QUASSIN, *v.* QUASSIA.

QUEBRACO or **QUEBRACHO BARK**, the bark of *Aspidosperma Quebracho*, obtained from the Argentine Republic *v.* VEGETO-ALKALOIDS.

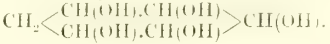
QUEEN'S METAL *v.* TIN.

QUEEN'S WARE *v.* POTTERY.

QUEEN'S WOOD *v.* BRAZIL WOOD.

QUERCETIN *v.* HORSE CHESNUT and QUERCITRON BARK.

QUERCITE is a pentahydric alcohol according to Homann (A. 190, 282) and Prunier (A. Ch. [5] 15, 1). Kanonnikow found that on reduction it was chiefly converted into aromatic compounds, and assigned to it the constitution—



$$CH_2<\begin{matrix}CH(OH).CH(OH)\\CH(OH).CH(OH)\end{matrix}>CH(OH).$$

If Kanonnikow's formula be correct, quercite is closely related to inosite, and on oxidation should yield similar products to those obtained from the latter by Maquenne (A. Ch. [6] 12, 1).

When quercite is treated with nitric acid of sp.gr. 1·39, first for 12 hours at 20°, and then for 36–48 hours at 30°, it yields mucic acid and trihydroxyglutaric acid, but no aromatic compounds could be obtained either by oxidation or any other chemical process. Only very small quantities of the two acids are formed, most of the quercite being converted into unstable compounds similar in behaviour to those obtained from sorbinose and levulose.

These results seem to show that quercite has not the constitution given to it by Kanonnikow (H. Kiliani and C. Scheibler, B. 22, 517–520; S. C. I. 8, 406).

QUERCITRIN *v.* GLUCOSIDES; also HORSE CHESNUT and QUERCITRON BARK.

QUERCITRON-BARK. This dye stuff is the inner portion of the bark of *Quercus citrina*, also called *Quercus tinctoria* and *Q. nigra*, a species of oak indigenous to the United States of America. The dark outer bark is removed and the remaining portion is rasped so as to form a mixture of woody fibre and fine powder, of a dull buff colour and possessing a bitter astringent taste. This dye stuff has been the subject of examination by several chemists, and although many discrepancies and contradictions occur in their published statements, and numerous formulæ have been assigned to the colouring principles discovered, still it seems to be firmly established that quercitron-bark contains essentially a glucoside, *quercitrin*, which, under the influence of boiling dilute mineral acids, is split up into the true colouring matter *quercetin*, and a sugar termed *isodulcite* or *rhamnose*.

Quercitrin is prepared, according to Liebermann and Hamburger, by treating the powdered bark for about 6 hours with 5–6 times its weight of 85 p.c. alcohol. After concentrating the filtered hot solution to one-half, a considerable quantity of glacial acetic acid is added, and impurities are precipitated by the addition of an alcoholic solution of lead acetate, avoiding excess. The lead compound of the impurities is insoluble in acetic acid, that of the quercitrin is soluble.

Any quercitrin which, through the use of lead acetate in excess, is precipitated along with the impurities, may be removed from the precipitate by boiling it with 10 p.c. acetic acid. With the right amount of lead acetate the precipitate is somewhat dense and of a pale-brown colour; with excess, it has a yellowish-brown appearance.

Having filtered off the lead precipitate of the impurities, the solution is treated with hydrogen sulphide, and the filtrate from the lead sulphide is evaporated to dryness to remove all acetic acid. The residue is dissolved in alcohol, then precipitated with water, and the quercitrin thus obtained is recrystallised four times from hot water, at first with the addition of animal charcoal. Thus prepared quercitrin forms minute pale-yellow needles, difficultly soluble in ether, almost insoluble in cold water, and very sparingly soluble even in hot water. It is readily soluble in alcohol, acetic acid, dilute caustic and carbonated alkalis. Its ammonia solution exposed to air becomes gradually of a dark-brown colour. Its aqueous and alcoholic solutions give with ferric chloride an intense dark-green colouration. Ammoniacal silver and gold salts are reduced. With lead acetate it gives a yellow precipitate soluble in acetic acid. It dyes mordanted cloth, but the colours obtained are weak compared with those yielded by the true colouring matter, quercetin.

According to Liebermann and Hamburger, when dried at 125–130°C. quercitrin has the formula $C_{36}H_{38}O_{20}$ (m.p. in air-bath about 135°).

Quercitrin potassium $C_{36}H_{36}K_2O_{20}$ is obtained as a yellow precipitate by mixing together perfectly cold concentrated alcoholic solutions of quercitrin and potassium hydrate. Exposed to air in the moist condition it rapidly becomes brown and resinous; when dry it forms a yellow powder, readily soluble in water, but little soluble in alcohol.

Tetrabromquercitrin $C_{36}H_{34}Br_4O_{20}$ is prepared by adding slowly, and in the cold, 4 parts bromine to 5 parts finely-powdered quercitrin suspended in glacial acetic acid so as to form a thick paste. Excess of acetic acid hinders the reaction. After twenty-four hours, with frequent stirring, the precipitate is collected on a filter, washed with alcohol, dried on porcelain, and recrystallised from hot alcohol. It forms pale-yellow crystalline granules readily soluble in alcohol, less so in glacial acetic acid and in ether, and very little soluble in chloroform; m.p. 229° with decomposition. It dyes aluminium mordanted cloth more orange shades of yellow than does quercitrin.

Acetyl and methyl derivatives of quercitrin have not been prepared in a form suitable for analysis.

Quercetin. On heating an aqueous solution of quercitrin with a little dilute sulphuric acid for about three hours on the water-bath, the solution becomes almost colourless, and the quercetin is thrown down as a bright-yellow precipitate consisting of minute star-shaped groups of needles. If the quercitrin employed was pure, the precipitate merely requires to be washed free from acid and dried. Quercitrin is insoluble in cold water, and very sparingly soluble even in hot water, but is more soluble in hot glacial acetic acid, from which it separates on cooling. In ether it is by no means so soluble as in alcohol, in which it readily dissolves, as also in alkalis. Its ammonia solution rapidly becomes brown when exposed to air. It melts with decomposition above 250°C. With ferric chloride its alcoholic solution gives a deep-green colour like that given by quercitrin, but on heating it becomes red. Silver nitrate rapidly reduces it even in the cold, gold chloride and Fehling's liquid only when heated. An alcoholic lead acetate solution gives an insoluble orange-red precipitate; barium hydrate gives a similar precipitate. Cold nitric acid colours it green, then red, and finally dissolves it with a red colour, but, on heating, it is decomposed with formation of oxalic acid, and, according to Zwenger and Dronke, also picric acid. At 50–60°C. concentrated sulphuric acid dissolves it with formation of a soluble sulphonic acid, which still possesses dyeing properties. Quercetin dyes mordanted cloth much better than quercitrin, giving purer and brighter colours.

Dried at the ordinary temperature over sulphuric acid, its formula, according to Herzig, is $C_{24}H_{16}O_{11} + 3H_2O$.

Dried at 130°C., Liebermann and Hamburger give its formula as $C_{24}H_{16}O_{11}$.

When quercetin is treated with caustic potash it gives different decomposition products, according to the temperature employed and the duration of the reaction.

If 1 part of quercetin is heated with 3 parts of potassium hydrate till a sample of the melt dissolved in water rapidly loses its yellow colour at the edges and changes to red, and a few drops of hydrochloric acid no longer produce a flocculent precipitate, three decomposition products are formed, viz., *paradatiscetin*, *quercetic acid*, and *phloroglucin*. Impure paradatiscetin precipitates in the form of yellow flocks from the acidified aqueous solution of the melt on cooling. The quercetic acid and phloroglucin are contained in the filtrate, from which they are extracted by means of ether, and ultimately separated from each other by lead acetate, which precipitates the former but not the latter.

If the melting with potassium hydrate is continued longer than is necessary to obtain quercetic acid—viz. till the melt when dropped into water dissolves with a dull-yellow colour, and more rapidly acquires a red colour than in the first instance—then a new substance termed '*quercimeric acid*' is produced. It is isolated in the same manner as quercetic acid, from which it differs by being much more soluble in water.

If the melting with potassium hydrate is continued still further, till an aqueous solution of the melt no longer acquires a red colour, then on acidifying with hydrochloric acid and shaking with ether, *protocatechuic acid* alone is extracted. This substance is also produced if quercetic or quercimeric acid is melted with potassium hydrate.

Paradatiscetin $C_{15}H_{10}O_6$ crystallised from dilute alcohol forms lustrous yellow needles, sparingly soluble in water. Ferric chloride colours its alcoholic solution a deep purple; bromine water gives a similar reaction. Lead acetate produces in its aqueous solution a yellow precipitate. Its yellow alkaline solution on exposure to air changes to a deep green.

Quercetic acid $C_{15}H_{10}O_7$ crystallises from water as colourless silky needles, readily soluble in alcohol and in ether, but little soluble in cold water. Its alkaline solution when exposed to air acquires a carmine-red colour. Ferric chloride colours its solution blue.

Quercimeric acid $C_8H_6O_5 + H_2O$ forms colourless granular crystals, very soluble in water, alcohol, and ether. Its alkaline solution rapidly acquires a deep reddish-purple colour. Generally speaking, its reactions are very similar to those of quercetic acid.

If a sodium hydrate solution of quercetin is treated with sodium-amalgam till the liquid changes from a deep brown to a brownish-yellow colour, then neutralised with hydrochloric acid and agitated with ether, the ether extracts phloroglucin and two other products, which may be separated by precipitating them with lead acetate. They differ from each other in their solubility in water. The least soluble product, having the composition $C_{13}H_{12}O_5$, crystallises in the form of minute prisms, and is readily soluble in alcohol and ether. Its alcoholic solution is coloured violet by ferric chloride, and violet changing to brownish-yellow by potash. By further reduction with sodium amalgam it is changed into phloroglucin; by fusion with caustic potash it yields phloroglucin and protocatechuic acid. The more soluble product $C_7H_8O_3$, m.p. 130°C., is obtained as granular crystals. Its aqueous solution is coloured deep orange-red by caustic alkali, green by ferric chloride, changing to violet on the addition of sodium carbonate. It reduces silver and alkaline cupric solutions, and on fusion with caustic potash yields protocatechuic acid.

An alcoholic solution of quercetin, acidified with hydrochloric acid, when treated with sodium amalgam rapidly acquires a purple colour; the solution then yields, on evaporation, a red crystalline substance (Stein's paracarthamin), analogous to the isomorin obtained in a similar manner from the colouring matter of old fustic. By exposing its alkaline alcoholic solution to air, it is readily oxidised and reconverted into quercetin. With alkalis it gives a green colour, which is changed to red by acids.

Octacetyl-quercetin $C_{21}H_8O_3(OC_2H_3O)_8$, m.p. 189°–191°, is obtained by heating for half an hour a mixture of quercetin 1 part, dehydrated sodium acetate $1\frac{1}{2}$ parts, and acetic anhydride 3–4 parts. After allowing the product to stand mixed with water for some time, all soluble matter is removed by washing, and the residue is crystallised from alcohol with the use of animal charcoal. It forms stellar groups of colourless silky needles, readily soluble in glacial acetic acid and in hot alcohol, sparingly soluble in cold alcohol and in ether, still less in carbon disulphide.

Tribrom-quercetin $C_{21}H_{13}Br_3O_{11}$ is prepared in the same way as the bromine compound of quercetin, employing 3 parts quercetin (1 mol.) and 2 parts bromine (2 mol.). From hot alcohol, containing a little glacial acetic acid, it crystallises in the form of pale-yellow needles, m.p. 236°C., with decomposition. It dyes mordanted cloth in shades somewhat redder than those given by quercetin.

Tribromoctacetyl-quercetin
$C_{21}H_5Br_3O_3(OC_2H_3O)_8$,
m.p. 218°–219°C., is prepared by heating a mixture of pure crystalline dibrom-quercetin with dehydrated sodium acetate and acetic anhydride. Crystallised from a mixture of absolute alcohol (2 parts) and glacial acetic acid (1 part), it forms tufts of colourless silky needles, m.p. 218°–219°C., slowly soluble in chloroform.

Tetrabrom-quercetin $C_{21}H_{12}Br_4O_{11}$ is prepared by suspending tetrabrom-quercitrin in water slightly acidified with dilute sulphuric acid, and heating on the water-bath for 2–3 hours. The product is washed free from acid and crystallised from a mixture of alcohol and acetic acid. It forms pale-yellow needles, slightly soluble in benzene, chloroform, and dilute alkalis. It differs from the dibrom-quercetin by its lesser solubility in cold alcohol and by dyeing mordanted cloth somewhat redder in shade.

Tetrabromdiacetyl-quercetin
$C_{21}H_{10}Br_4O_9(OC_2H_3O)_2$,
is prepared from tetrabrom-quercetin in the same way as tribromoctacetyl-quercetin is obtained from tribrom-quercetin; but it differs from these by its higher melting-point 226–228°C., and its exceedingly slight solubility in cold alcohol. It is very readily soluble in glacial acetic acid, soluble in hot alcohol, sparingly soluble in chloroform and carbon disulphide.

Pentabromoctacetyl-quercetin
$C_{21}H_4Br_5O_3(OC_2H_3O)_8$
is made by first treating a glacial acetic acid solution of quercitrin with excess of bromine, and then decomposing the product by sulphuric acid; or quercetin is treated with dry bromine. The pentabrom-quercetin thus obtained is changed into the octacetyl derivative in the usual manner. It crystallises from glacial acetic acid, in which it is sparingly soluble, in long needles, m.p. 251–253°.

Amido-quercetin is obtained as a brown amorphous substance by heating quercetin with ammonia in a sealed tube to 145–150°C., or by allowing the mixture to stand in the cold for about two months. It is soluble in alcohol, ether, ammonia, and hydrochloric acid, but is little soluble in water.

Pentaphenylcarbamin-quercetin
$C_{21}H_{11}O_6[NH(C_6H_5)CO_2]_5$.
is prepared by the action of phenylcarbimid on quercetin at 160°C. The product is washed first with cold benzene and then with boiling alcohol. It is an insoluble amorphous substance, m.p. 200–205°C.

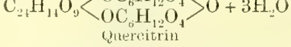
Quercetin-sodium $C_{21}H_{14}O_9(ONa)_2$ is prepared by dissolving sodium carbonate (5 parts) and quercetin (1 part) in a little hot water, and leaving the filtered dark-red solution in a stoppered vessel. After some time, microscopic yellow needles are precipitated, which, when exposed to air, rapidly become discoloured.

Quercetin-barium is precipitated, as an orange-red precipitate of variable composition, on adding barium hydrate to a concentrated aqueous solution of quercetin-sodium. According to Liebermann and Hamburger, its composition is $2C_{24}H_{14}BaO + BaO$.

Benzoyl-quercetin has not yet been obtained in a crystalline condition.

Isodulcit $C_6H_{14}O_6$, is obtained from quercitrin by decomposing it with hot dilute sulphuric acid, and proceeding exactly in the same way as when preparing it from the xanthorhamnin of Persian-berries. By mixing an alcoholic solution of isodulcit with sodium-alcohol, white crystalline sodium-isodulcit $C_6H_{12}O_4(ONa)_2$ is obtained.

Liebermann and Hamburger represent the decomposition of quercetin by acid as follows:



$$\underset{\text{Quercitrin}}{C_{24}H_{14}O_9{<}\begin{matrix}OC_6H_{12}O_4\\OC_6H_{12}O_4\end{matrix}{>}O} + 3H_2O$$

$$= \underset{\text{Quercetin}}{C_{24}H_{16}O_{11}} + 2\underset{\text{Isodulcit}}{[C_6H_{12}O_4.(OH)_2]}.$$

In consequence of the composition of the acetyl and sodium compounds of quercetin, Liebermann and Hamburger consider it to contain two hydroxyl groups.

When quercetin is heated with concentrated hydrochloric acid at 140–150°C. in a sealed tube, no methyl or ethyl chloride is produced; hence it does not contain methoxyl or ethoxyl groups.

Hexa-ethyl quercetin $C_{24}H_{10}(OC_2H_5)_6O_5$ is prepared by heating in a sealed tube for 12 hours, at 100°C., a solution of 1 mol. quercetin in 4–5 mol. alcoholic potash, with a corresponding amount of ethyl iodide. After distilling off the excess of alcohol and ethyl iodide the residue is mixed with water.

The insoluble portion is washed, dried, and dissolved in hot alcohol. Caustic potash is added to the concentrated solution, and on cooling, the potassium compound of the ethyl derivative is precipitated. This is washed with alcohol, then with slightly acidified water, in order to remove the potash, and is finally crystallised from hot alcohol in the form of long yellow needles, m.p. 120–122°; insoluble in caustic potash; yield 50–55 p.c.

In consequence of this ethylquercetin not being decomposed during the prolonged heating at 100°C., there being produced only its potassium compound, it is improbable that quercetin contains carboxyl groups. By employing, however, a temperature of 140-150°C. a smooth decomposition is effected; and after distilling off excess of alcohol, and acidifying with sulphuric acid, a colourless crystalline substance separates, which, when purified and crystallised from hot alcohol, forms stellar groups of lustrous needles, m.p. 165–166°C. Analyses of its barium, calcium, and sodium salts, and the production of its ethyl-ether derivative, with m.p. 56–57°C., prove it to be di-ethyl-protocatechuic acid. Other substances produced at the same time show, when heated with hydrochloric acid, the phloroglucin reaction; they probably contain an ethyl derivative of phloroglucin. The amount of di-ethyl protocatechuic acid thus obtained in the foregoing experiments corresponds approximately to the production of 2 mols. from 1 mol. of hexa-ethyl quercetin; hence Herzig concludes that quercetin contains the residues of 2 mols. protocatechuic acid.

Hexa-methyl-quercetin $C_{24}H_{10}(OCH_3)_6O_5$ is prepared like the corresponding ethyl derivative. The dried product of the reaction is dissolved in benzene, whereby brown tarry impurities remain undissolved. After distilling off the benzene, the residue is crystallised from alcohol in the form of lustrous yellow needles; m.p. 156–157°C. Treated with alcoholic potash at 100°C. it yields its potassium compound, but at a higher temperature it is decomposed, and yields dimethyl-protocatechuic acid; m.p. 180°C.

Diacetyl-hexa-methyl quercetin
$C_{24}H_8(OCH_3)_6(OC_2H_3O)_2O_3$
is obtained by heating hexamethyl quercetin with acetic anhydride (8 to 10 parts) and dehydrated sodium acetate for 3 to 4 hours. Crystallised from absolute alcohol it forms colourless lustrous needles; m.p. 167–169°C.; very similar in appearance to the acetyl derivative of quercetin.

Diacetyl-hexa-ethyl quercetin, formed in a similar manner, is also a colourless compound.

Since the hexa- methyl and ethyl derivatives of quercetin retain the yellow colour characteristic of quercetin itself, it probably shows, according to Herzig, that they are true derivatives of the latter, whereas his opinion is that in the colourless acetyl derivative of quercetin the acetyl group has entered into the quercetin more deeply, and is not indicative of the true substitution of two hydroxyl groups by acetyl, and he thinks the production of colourless diacetyl derivatives of hexa-methyl quercetin support this view. Herzig concludes that quercetin contains at least six free hydroxyl groups.

As the result of his latest researches, Herzig states that there are not present in the quercetin molecule two quinone oxygen atoms, as he formerly supposed. The molecular weight of quercetin he has experimentally determined as 294, with which the formula $C_{15}H_{10}O_7$ best accords. Rhamnetin, the colouring matter of Persian-berries, he now looks upon as mono-methyl-quercetin, while quercetin itself he regards as an oxy- derivative of the colouring-matter of young fustic, *i.e.* as an oxy-fisetin. To fisetin he assigns the formula $C_{15}H_{10}O_6$. In support of this view he advances the fact that when fisetin is oxidised by means of atmospheric oxygen it yields protocatechuic acid and resorcinol, while under the same influence quercetin gives protocatechuic acid and phloroglucin.

Commercial Preparations.

Flavin. This is the most important commercial preparation of quercitron-bark; it seems to have been first imported to this country from America. The details of its manufacture have been guarded with much secrecy, and analyses of commercial samples show that different methods have been adopted by different makers. Some specimens consist essentially of quercitrin, while others contain only quercetin. The former have probably been prepared by merely extracting the bark with water and high-pressure steam, or, as it is said, with steam only, at a temperature of 102–103°. In some cases it would appear as if the flavin were merely ground quercitron-bark mechanically purified by a process of sifting.

The best qualities of flavin, however, are those in which the colouring matter is present as more or less pure quercetin, and entirely free from woody fibre. Such genuine flavin is prepared by rapidly extracting the powdery portion of rasped quercitron-bark with ammonia or other alkali, and at once acidifying the solution with sulphuric acid in order to avoid deterioration of the colouring matter by atmospheric oxidation. After allowing the acid solution to stand for some time a worthless flocculent precipitate is filtered off, and the filtrate is boiled. The precipitate thus produced is ultimately collected, washed with cold water till free from acid, and finally dried. Good flavin of this character has about sixteen times the tinctorial value of quercitron-bark. It is not very soluble, but it yields with aluminium and especially with tin mordants, much more brilliant colours than does quercitron-bark.

Patent-bark, or 'commercial quercetin,' is a preparation of quercitron-bark analogous to the garancin made from madder. It is manufactured in a similar manner, viz. by boiling, for about 2 hours, 100 parts finely-ground quercitron bark, 300 parts water, and 15 parts concentrated sulphuric acid. The product is collected on a filter, washed free from acid, and dried. The yield is about 85 p.c. of the bark employed, while its colouring power is two and a half times greater. It seems to have been first manufactured in 1855 by Leeshing.

Bark-liquor is simply an aqueous extract of quercitron-bark, and is sold with a sp.gr. of 1·06° to 1·255°.

Application.—Quercitron-bark, patent-bark, and bark extracts are chiefly employed by the calico and woollen printer. The latter are used in the preparation of steam-yellows, olives, chocolates, &c., in conjunction with aluminium, tin, chromium, and iron mordants. The former were at one time largely employed in conjunction with garancin, for the production of various compound shades, *e.g.* chocolate, dull red, orange, &c. Now they may be used in a similar manner along with alizarin. When used alone, quercitron-bark and patent-bark give, with aluminium mordant yellow, with tin orange, with chromium olive-yellow, with iron greenish-olive.

Flavin is used chiefly in wool dyeing for the production, in single-bath, of bright yellow and orange fast to milling, or along with cochineal to obtain a bright scarlet. The mordant employed is stannous chloride and oxalic acid or cream of tartar.

On cotton all the quercitron colours are but moderately fast to light; on wool and silk the chromium, copper, and iron colours are fairly fast, whereas the aluminium and tin colours are only moderately so.

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J. J. H.

QUICKSILVER *v.* Mercury.

QUICK VINEGAR PROCESS *v.* Acetic acid.

QUINALDINE *v.* Quinoline.

QUINCE GUM *v.* Gums.

QUINIDINE *v.* Vegeto-alkaloids.

QUININE *v.* Vegeto-alkaloids.

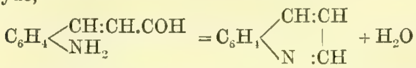
QUINIZARIN. 1:4-*Dioxanthraquinone* *v.* Alizarin and allied colouring matters.

QUINOL *v.* *Hydroquinone*, art. Phenol and its homologues.

QUINOLINE. *Leucoline* C_9H_7N.

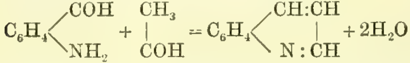
History.—Runge in 1834 isolated from coal-tar an oil which was termed 'leukol' to distinguish it from 'kyanol' (aniline), since, unlike the latter, it gave no colour on treatment with bleaching-powder solution (P. 31, 68). Gerhardt, in 1842, obtained a basic substance 'chinoilin' or 'chinolein' by distilling quinine (A. 42, 310), cinchonine, and strychnine with caustic potash (A. 44, 279; *cf.* Wyschnegradsky, quoted by Krakau, B. 13, 2318), and the identity of leucoline with quinoline was established three years later by Hofmann (A. 47, 76; 53, 427), whose conclusions have been verified by the later researches of Hoogewerff and van Dorp (Rec. trav. chim. 1, 1). The quinoline, both from coal-tar and cinchonine, is not a pure substance, since it contains quinaldine (Traub, B. 16, 297, 878; Jacobsen and Reimer, B. 16, 1084; Traub and Schärges, B. 17, 2618; Krakau, B. 18, 1934); coal-tar quinoline (b.p. 235–240°) containing, in addition to 20–25 p.c. of quinaldine (*cf.* Jacobsen, Germ. Pat. 23967; Actieng. f. Anilinfab., Germ. Pat. 40420), a noteworthy quantity of isoquinoline (Hoogewerff and van Dorp, Rec. trav. chim. 4, 125).

Formation.—Quinoline is obtained by the distillation of cinchonic acid with lime (Koenigs, B. 12, 98). Synthetically it has been prepared by the condensation of orthamidocinnamic aldehyde,



$$C_6H_4\left<\begin{matrix}CH{:}CH.COH\\ NH_2\end{matrix}\right. = C_6H_4\left<\begin{matrix}CH{:}CH\\ |\\ N\ \ {:}CH\end{matrix}\right. + H_2O$$

(Baeyer and Drewsen, B. 16, 2207); by passing allylaniline over heated lead oxide (Koenigs, B. 12, 453); by warming a dilute aqueous solution of orthamidobenzaldehyde and acetaldehyde with a few drops of aqueous caustic soda



$$C_6H_4\left<\begin{matrix}COH\\ \\ NH_2\end{matrix}\right. + \begin{matrix}CH_3\\ |\\ COH\end{matrix} = C_6H_4\left<\begin{matrix}CH{:}CH\\ |\\ N{:}CH\end{matrix}\right. + 2H_2O$$

(Friedländer and Gohring, B. 16, 1835); by the dry distillation of acroleinaniline (Koenigs, B. 13, 911); and by heating a mixture of aniline, glycerol, and sulphuric acid (Koenigs, B. 13, 912), preferably with nitrobenzene (Skraup, M. 1, 317).

Preparation.—24 parts of nitrobenzene, 38 parts of aniline, 120 parts of glycerol, and 100 parts of concentrated sulphuric acid, are mixed together in a reflux apparatus, shaken until the whole of the aniline sulphate is dissolved, and either carefully heated until the vigorous reaction sets in, or warmed for a day at 125–130°, and afterwards heated at 180–200° to complete the reaction. After dilution with water, any nitrobenzene is removed by steam-distillation, the residual liquor rendered alkaline, and the separated base distilled with steam, fractionated to remove the greater part of the aniline, and freed from the remainder by treatment either with potassium bichromate in sulphuric acid solution or with nitrite in acid solution and subsequent steam-distillation from alkaline solution. The yield amounts to about 60 p.c. of the theoretical (Skraup, M. 2, 141). As prolonged digestion (36 hours) at the temperature of reaction has been found to result in the complete conversion of the toluidines into toluquinolines, thus rendering the purification with bichromate or nitrite unnecessary (Nölting and Trautmann, B. 23, 3654), it is to be expected that equally good results are to be obtained in like manner in the preparation of quinoline and quinoline derivatives generally.

Properties.—It is a colourless oily liquid, which boils at 237·1 under 746·8 mm. (Skraup), at 238° under 760 mm. (Kahlbaum), at 234–234·5 under 758·6 mm. pressure (Schiff, B. 19, 566), and has a sp.gr. = 1·0965 at 11·5° (Oechsner, A. Ch. [5] 27, 487) and 1·0947 at 20° (Skraup). It has a disagreeable penetrating odour, a bitter acrid taste, and is dissolved sparingly by water, but readily by alcohol, ether, carbon bisulphide, &c.

Reactions.—(1) Quinoline is oxidised with difficulty by chromic acid mixture, but on treatment with potassium permanganate in alkaline solution is converted into *quinolinic* (2:3-pyridinedicarboxylic) acid, oxalic acid, ammonia, and carbon dioxide (Hoogewerff and van Dorp, B. 12, 747, 983; Skraup, M. 2, 147).

(2) Nitration with nitro-sulphuric acid results in the formation of a mixture of ortho- and ana- nitroquinoline, and of two dinitroquinolines (Koenigs, B. 12, 449; Claus and Krämer, B. 18, 1243; *cf.* Nölting and Trautmann, *l.c.*).

(3) The action of sulphuric acid on quinoline does not seem to be satisfactorily established. When heated with 7 parts of ordinary sulphuric acid at 220–230°, quinoline yields the orthosulphonic acid, but at 275–280° for twenty-four hours exclusively the parasulphonic acid, the ortho- and ana- acids being converted into the para-acid by heating with 4 parts of ordinary acid at 275–280° (Georgievics, M. 8, 577, 639; Bad. Anilin & Sodafab. Germ. Pat. 40901 of March 5, 1887). According to Claus, sulphonation with 10–20 p.c. anhydrosulphuric acid at 125–130° gives a mixture of the ortho-, meta-, and ana-acids, and at 170–180°, a mixture of the ortho- and ana-acids (J. pr. [2] 37, 261); La Coste and Valeur state that the ortho- and ana- acids are formed by the action of 3½ parts of 'fuming' sulphuric acid at 170° for one hour (B. 20, 95); Bedall and O. Fischer found that by heating with 'fuming' sulphuric acid a mixture of ortho- and ana-[1] acid was produced (B. 15, 683, 1979) in proportions which with Nordhausen acid varied with the temperature (about four times as much ortho- as ana- being present at temperatures below 200°, the ana- becoming chief product at 270°), or with the temperature at 120° varied with the amount of dissolved anhydride (Riemerschmied, B. 16, 721); and finally, Lellmann arrives at the conclusion that a mixture of a second (pseudo-) ana- acid with the ortho- acid is obtained when quinoline is heated with 5 parts of anhydrosulphuric acid containing 1 part of anhydride dissolved in 2 parts of ordinary sulphuric acid at 180°; that the yield of pseudana-acid increases at temperatures up to 260°, and that the pseudana- acid is identical with the ana- acid obtained by Skraup's method from metamidobenzenesulphonic acid (B. 20, 2172). The mixture of ortho- and ana- acid on further sulphonation with 2 parts of Nordhausen acid at 250° for eighteen hours yields a mixture of two disulphonic acids, both of which are produced from the ortho- acid under like conditions (La Coste and Valeur, B. 19, 996; 20, 98; La Coste, Germ. Pat. 29920 of April 20, 1884, expired Sept. 1886).

These sulphonic acids yield hydroxyquinolines on fusion with caustic potash, and it is to be noted that Lellmann's pseudana-acid appears to give the same 4-hydroxyquinoline as that obtained from Riemerschmied's ana- acid (Lellmann, *l.c.*), although the nitriles from the two sources appear to differ (Lellmann and Reusch, B. 21, 397).

(4) On reduction with tin or zinc and hydrochloric acid quinoline is converted into the *tetrahydro-* derivative, the four atoms of hydrogen being taken up by the 'pyridine-ring' (Wyschnegradsky, B. 12, 1481; 13, 2400). An amorphous solid is also formed in the reaction. By reduction with hydriodic acid and amorphous phosphorus at 230° tetrahydroquinoline yields a product containing 8 p.c. *hexahydroquinoline*, 55 p.c. of *decahydroquinoline*, a third base not volatile with steam, and 0·25 p.c. of a hydrocarbon, possibly propylhexamethylene (Bamberger and Lengfeld, B. 23, 1138).

(5) Quinoline is a strong tertiary base, and forms addition products with methyl chloride, methyl iodide, &c. The *methiodide* C_9H_7N,CH_3I crystallises in large, sulphur-yellow forms, melts

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[1] Termed 'meta-' by these chemists.

at 72° (La Coste, B. 15, 192), and, like compounds of this character, is converted into a strongly alkaline base on treatment with moist silver oxide. Crystalline addition compounds of quinoline, quinoline metho-chloride, &c., with iodine chloride have been prepared (Chem. Fabrik auf Actien. (vorm. E. Schering), Germ. Pat. 30358, of Mar. 9, 1884; expired July 1886; Eng. Pat. 9252, of 1884), and of these the quinoline-chloriodide was proposed as an iodoform substitute under the name 'quinoiodine.'

Salts.—The *hydrochloride*, C_9H_7N,HCl, forms very soluble deliquescent crusts; the *zincochloride*, crystallises in sparingly-soluble needles, and the *platinichloride*, $(BHCl)_2,PtCl_4+2H_2O$, forms small sparingly-soluble orange-yellow needles melting at 218° (Lellmann and Alt, A. 237, 323). The *picrate* crystallises from benzene in small bright-yellow needles melting at 203°; the *chromate*, $B_2,H_2Cr_2O_7$, crystallises from hot water in characteristic lustrous yellow needles melting at 164–167° (Hoogewerff and van Dorp, Rec. trav. chim. 1, 13); the *tartrate* $B_3(C_4H_6O_6)_4$ crystallises from alcohol in large flat needles (Friese, B. 14, 2805); and the *salicylate*, $B,C_7H_6O_3$, forms a reddish-grey powder (Friese).

Tetrahydroquinoline $C_9H_{11}N$.

Formation.—Tetrahydroquinoline is obtained from quinoline by the action of zinc and hydrochloric acid (Wyschnegradsky, B. 12, 1481), tin and hydrochloric acid (*ibid.* B. 13, 2400), sodium amalgam (Koenigs, B. 14, 100), or sodium (Weidel and Gläser, M. 7, 328); also from carbostyril by reduction in boiling alcoholic solution with sodium (Knorr and Klotz, B. 19, 3302).

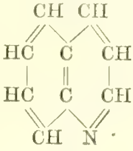
Preparation.—Quinoline is dissolved in about 30 parts of strong hydrochloric acid, and treated gradually on a water-bath with 3–3·5 parts of granulated tin. The excess of acid is removed by evaporation, the residue rendered alkaline, and the tetrahydroquinoline and unreduced quinoline separated from the solid amorphous reduction-product by steam distillation. To free the tetrahydro- base from quinoline the dry ethereal solution of the two is saturated with gaseous hydrogen chloride, and the precipitated tetrahydroquinoline hydrochloride crystallised from boiling alcohol (Hoffmann and Koenigs, B. 16, 728).

Properties.—It crystallises in needles in a freezing mixture, but is an oil at the ordinary temperature, and boils at 244–246° under a pressure of 724 mm. The *hydrochloride* crystallises from water in readily soluble prisms, and from alcohol in slender prisms, melting at 180–181°. Methyl and ethyl iodide react vigorously with the base, forming 1′-alkyl derivatives, of which 1′-methyltetrahydroquinoline was at one time employed in the form of acid sulphate as an antipyretic, under the name

Kairoline. This base, $C_9H_{10}.NMe$, is obtained either by direct methylation of tetrahydroquinoline (Hoffmann and Koenigs, B. 16, 732), or more readily by gradually adding 1·5 parts of granulated tin to a solution of 1 part of quinoline methiodide in 10 parts of concentrated hydrochloric acid (Feer and Koenigs, B. 18, 2388). It boils at 242–244° under a pressure of 720 mm., forms deliquescent salts, and exhibits a marked analogy with dimethylaniline.

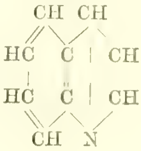
CONSTITUTION OF QUINOLINE.

Körner's suggestion that the quinoline molecule contains a benzene and a pyridine nucleus having two carbon atoms in common,



I.

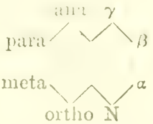
or



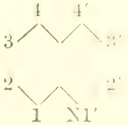
II.

is generally accepted, in view of the formation of quinoline derivatives by the condensation (*a*) of orthamidobenzaldehyde with acetaldehyde, and (*b*) of orthamidocinnamic aldehyde, and derives confirmation from the fact that quinoline on oxidation with potassium permanganate in alkaline solution yields 2:3-pyridinedicarboxylic (quinolinic) acid (Hoogewerff and van Dorp, B. 12, 747, 983; Skraup, M. 2, 147), whilst quinaldine, which can be obtained by corresponding syntheses from (*a*) orthamidobenzaldehyde and acetone, and (*b*) orthamidobenzilidenacetone, yields, under like conditions, acetorthamidobenzoic acid (Döbner and v. Miller, B. 15, 3077). As pointed out by Bamberger (A. 257, 21; C. J. 58, 1302), the two ring systems are not *identical* with, but only *similar* to, those of benzene and pyridine respectively, each becoming identical, however, with that of benzene or pyridine, as the case may be, when the second ring is destroyed by oxidation or its influence is removed by reduction (*cf.* Bamberger, A. 257, 20; C. J. 58, 1302). Which of the two formulæ, I. or II., expresses the constitution of quinoline is still a matter of controversy, and it is possible that some quinoline derivatives may have the first, others the second, formula. Indeed, Lellmann claims to have established the existence of two isomeric ana- (or 4-) quinoline-carboxylic acids (Lellmann and Alt, A. 237, 325), -sulphonic acids (Lellmann, B. 20, 2172), and -nitriles (Lellmann and Reusch, B. 21, 397), and refers the isomerism to the presence in the one, and absence in the other series of a para- linkage between carbon and nitrogen in the 'pyridine-ring.'

Conventionally quinoline is represented by a double hexagon having one side in common, carbon atoms being supposed to be placed at each of the angles except the one against which N is written, and with the exception of the two 'central' carbon atoms, associated each with an atom of hydrogen. To indicate the orientation of a substituent the positions have been distinguished thus—



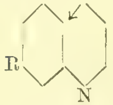
III.



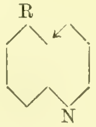
IV.

System III., adopted by Skraup (M. 7, 157), is generally used on the Continent; system IV. is employed in the Chemical Society's publications and in a modified form by Baeyer and his pupils, who number the positions in the 'benzene-ring' 1, 2, 3, 4, and in the 'pyridine-ring' N, 1, 2, 3, indicating by the abbreviations 'Bz' or 'Py' whether the substituent occurs in the 'benzene' or 'pyridine' nucleus (B. 17, 960).

Orientation in the quinoline series is usually determined by oxidation, one or other of the rings being destroyed, with the production either of a substituted phthalic acid, or of a substituted 2:3-pyridinedicarboxylic (quinolinic) acid (*cf.* v. Miller, B. 23, 2252; 24, 1900). Difficulty arises, however, in those cases in which the ring containing the substituent is oxidised away, but in many instances the position is determined by the synthetical method employed in the preparation of the compound; thus in Skraup's reaction ortho- and para- substituted anilines can only yield ortho- and para-substituted quinolines respectively. From meta- substituted anilines, however, either meta- or ana- quinoline derivatives result, according as ring-formation ensues in the para- or ortho-position to the substituent, thus—

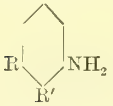


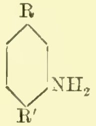
(meta-)



(ana-)

but, as Skraup and Brunner (M. 7, 139), Tortelli (G. 16, 366), and Lellmann and Alt (A. 237, 315), have shown, it is possible to determine which isomeride is formed by comparison with the quinoline derivatives obtained by submitting one or other of the disubstituted anilines containing a second radicle R′ (COOH or Br in the experiments quoted) in the positions





to the Skraup reaction, and subsequently displacing the radicle R′ by hydrogen. In this way the meta- and ana- quinolinecarboxylic acids have been identified, and these serve as reference compounds for quinoline derivatives of either series, which by the usual reactions can be converted into them.

With regard to the formation of the meta- and ana- isomerides, it may be noted that in those cases in which both have been found in the product one is always present in much larger proportion than the other. The evidence at disposal tends to show that anilines containing positive radicles, such as metatoluidine and metamidophenol, yield the meta- isomeride, and anilines containing negative radicles, such as metamidobenzoic acid and metamidobenzenesulphonic acid, yield the ana- isomeride as chief product.

Uses of Quinoline Derivatives.

In addition to their limited use in the manufacture of dye stuffs (*v. infra*) quinoline derivatives have been employed as antipyretics, the recognition of the fact that the cinchona alkaloids are derivatives of quinoline having led to the preparation and therapeutic investigation of many quinoline compounds. Quinoline having but feeble antipyretic properties (*cf.* Donath, B. 14, 178), attention appears to have been specially directed to its tetrahydro- derivatives, because on the one hand McKendrick and Dewar's investigations had shown that physiological activity was greater in those bases of the pyridine and quinoline series which contained the larger proportion of hydrogen (Pr. 22, 290), and on the other because Koenigs in his earlier researches was inclined to regard quinine and cinchonine as derivatives of 1′-methyltetrahydroquinoline (B. 14, 1857). This substance, prepared first by Hoffmann and Koenigs (B. 16, 731), was indeed found to be an antipyretic of some value, and was introduced as a quinine substitute under the name 'kairoline.'

The molecular formula of quinine differs from that of cinchonine by CH_2O, and Skraup's discovery of the fact that this difference is due to the presence of methoxyl in the para- position in the quinoline nucleus of quinine (M. 4, 697) naturally directed attention to the hydroxy- and methoxy- derivatives of tetrahydroquinoline, with the result that in antipyretic action the relation of orthohydroxy-1′-methyltetrahydroquinoline ('kairine') and of paramethoxytetrahydroquinoline ('thalline') to tetrahydroquinoline was found to be similar to that of quinine to cinchonine, a later observation of Einhorn's that paramethoxy-2′:4′-dihydroxydihydroquinoline far exceeds 2′:4′-dihydroxydihydroquinoline in antipyretic power (Germ. Pat. 55119 of May 20, 1890) affording further evidence in favour of this rule.

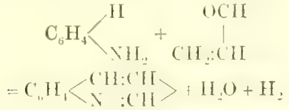
In the course of these investigations many results of considerable interest in reference to the relation between chemical constitution and physiological action were accumulated. Thus Filehne (quoted in the papers of O. Fischer (B. 16, 719) and Hoffmann and Koenigs, *l.c.*) found that orthohydroxy- and orthomethoxy-quinoline are poisonous, that their tetrahydro-derivatives, together with tetrahydroquinoline, exhibit a certain resemblance to quinine, but produce unpleasant subsidiary effects, and that their 1′-methyl or -ethyl derivatives, obtained by substituting the alkyl radicles for H in the chemically reactive NH-group, have a pronounced antipyretic action unaccompanied by the local action and objectionable after-effects noticed with the parent tetrahydro- bases. Again para-hydroxytetrahydroquinoline is poisonous, but loses its poisonous properties and is converted into the antipyretic 'thalline' when the H of the OH-, not of the NH-, radicle is replaced by methyl; thalline also being physiologically much more active than paramethoxyquinoline, the unreduced base (Jaksch, quoted by Skraup, M. 6, 773).

Later investigations have modified the views formerly held with reference to the nature of the quinoline nucleus in quinine—the ethylpyridine and not the quinoline constituent of the molecule being now regarded as more probably the hydrogenated portion of the molecule (Comstock and Koenigs, B. 20, 2510; Skraup, M. 9, 822)—and these added to the discovery of marked antipyretic properties in antipyrine and even in acetanilide (antifebrin) seem to have led to the abandonment of this line of research. During its continuance, however, many synthetical methods were devised for the preparation of quinoline derivatives, but mention can only be made of those which have the most general application.

Syntheses of Quinoline Derivatives.

(i.) *Preparation of derivatives containing radicles substituted in the 'benzene-nucleus.'* The most general of all the synthetical methods is that of Skraup which serves for the preparation of derivatives containing the substituent in the 'benzene-ring.' This method owes its origin to the discovery of alizarin-blue by Prud'homme in the course of some experiments having for their object the preparation of a nitroalizarin 'vat' by means of glycerol and sulphuric acid (Z. chem. Grossg. 2, 462). Graebe's investigation of alizarin-blue, obtained in addition to other products by heating nitroalizarin with these substances, proved it to be a quinoline derivative resulting from the condensation of molecular proportions of glycerol and nitroalizarin (B. 11, 522; A. 201, 333). Koenigs, who had previously obtained quinoline by passing allylaniline over heated litharge (B. 12, 453), and by dry distillation of acrolein-aniline (B. 13, 911), found that it could be obtained in small quantity by heating nitrobenzene—or better aniline—with glycerol and sulphuric acid (B. 13, 912). In these experiments, however, he was just anticipated by Skraup (M. 1, 317), who discovered that not only was quinoline produced by heating aniline with glycerol and sulphuric acid, in accordance, possibly, with the equations—

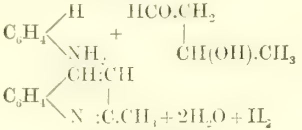
$$CH_2OH.CHOH.CH_2OH = CH_2:CH.CHO + 2H_2O$$



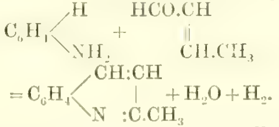
but also that the yield was very considerably increased by the addition of nitrobenzene. The extension of the method to homologues of aniline in the presence of the corresponding nitro-derivatives followed (Skraup, M. 2, 139; Schloesser and Skraup, M. 2, 518), the later discovery of La Coste that the nitro- derivative, as a rule, is not reduced to the corresponding amido- compound (*cf.*, however, Skraup, B. 15, 897), and that, consequently, any nitro- derivative, by preference nitrobenzene, can be employed in all cases as the oxidising agent (B. 15, 558), ensuring its application to all derivatives of primary aromatic amines. Quinoline derivatives containing the radicles Cl (La Coste, B. 15, 557), NO_2 (La Coste, B. 16, 669; Nölting and Trautmann, B. 23, 3667), NH_2 (Marckwald, B. 23, 1021), OH (Skraup, B. 15, 893; M. 6, 761; Germ. Pat. 14976 of Feb. 16, 1881, Eng. Pat. 678 of 1881; Bad. Anilin- & Sodafab., Germ. Pat. 28324 of Nov. 11, 1883), CH_3 (Skraup, M. 2, 152; 3, 381; Skraup and Brunner, M. 7, 139; Nölting and Trautmann, *l.c.*), COOH (Schloesser and Skraup, *l.c.*; Lellmann and Alt, A. 237, 319), and SO_3H (Farbw. Meister, Lucius & Brüning, Germ. Pat. 26430 of Aug. 3, 1883; Happ, B. 17, 192; Lellmann and Lange, B. 20, 1446; Nölting and Frühling, B. 21, 3156) in the 'benzene ring,' can therefore be readily obtained from the corresponding substituted anilines, the method being similar to that given under quinoline, except as regards the temperature at which reaction ensues. The yields are almost invariably good.

(ii.) *Preparation of alkyl derivatives containing the alkyl radicle in the 'pyridine-ring.'*—(1) The substitution of other polyhydric alcohols for glycerol in Skraup's reaction followed naturally on the publication of Skraup's paper. Erythrol and mannitol in Skraup's hands gave unpromising results (B. 15, 898), but from a mixture of aniline and nitrobenzene with glycol and sulphuric acid, Döbner and v. Miller obtained quinaldine (B. 14, 2813), a like result obtaining in the case of paraldehyde, acetal (*l.c.*), and lactic acid (Wallach and Wüsten, B. 16, 2007). The reaction is due to the formation of and condensation with acetaldehyde under these conditions, since ordinary aldehyde, like these substances, gives a good yield of quinaldine when digested with aniline and concentrated hydrochloric acid, the employment of nitrobenzene and sulphuric acid being unnecessary (B. 16, 2465). In all probability aldol first results, and either this or, more probably (Döbner and v. Miller, B. 17, 1721; *cf.* v. Miller, B. 24, 1720), crotonic aldehyde reacts with the amine thus:

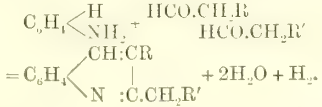
(*a*)



(*b*)



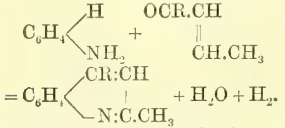
The reaction is a general one for all aldehydes of the general formula $R.CH_2.CHO$ (v. Miller, B. 18, 3360), or unsaturated aldehydes of the general formula $RCH_2.CH:CR'.CHO$, and leads to the production either of 2′ or 2′:3′- derivatives of quinoline, since the carbon atom of the aldehyde radicle always replaces H of the benzene nucleus, and not H of the NH_2 group of the amine, thus:



Dihydroquinolines, no doubt, first result, just as they probably do in the Skraup synthesis, but the tendency to produce quinolines is sufficiently great to ensure the elimination of the hydrogen, and addition of an oxidising agent is unnecessary. As shown by Döbner and v. Miller (B. 17, 1698), a portion of the aldehyde is reduced to the corresponding alcohol, which in presence of the acid acts upon the amine, forming an alkyl derivative, whilst a portion of the quinaldine also becomes reduced to the tetrahydro- derivative. With substituted anilines, such as amidophenols and amidobenzoic acids, quinaldines containing substituents in the 'benzene ring' are obtained (Döbner and v. Miller, B. 17, 939, 1705; Chem. Fab. auf Actien. (vorm. E. Schering), Germ. Pat. 24317 of Aug. 19, 1882, 29819 of Oct. 2, 1883), and with reference to these it may be noted that meta- derivatives of aniline seem to give exclusively meta- and not ana- derivatives of quinaldine (Döbner and v. Miller, B. 16, 2471; Harz, B. 18, 3398).

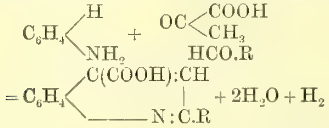
The method was extended to β-hydroxyketones by Beyer (J. pr. [2] 31, 48; 32, 127; 33, 395), who showed that quinaldine derivatives were also obtained with a mixture of a ketone and aldehyde in molecular proportions, an aldol being probably formed as intermediate product in this case also:

$$CH_3.CHO + CH_3.CO.R = CH_3.CH(OH).CH_2.CO.R$$
$$= CH_3.CH{:}CH.CO.R + H_2O$$



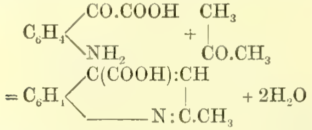
$$C_6H_4\left\langle\begin{array}{l}H\\NH_2\end{array}\right. + \begin{array}{l}OCR.CH\\\quad\|\\CH.CH_3\end{array}$$
$$= C_6H_4\left\langle\begin{array}{l}CR{:}CH\\\quad|\\N{:}C.CH_3\end{array}\right. + H_2O + H_2.$$

A similar condensation, with the production of carboxylic acids, ensues when pyruvic acid, an aldehyde and aniline are warmed together in alcoholic solution:



$$C_6H_4\left\langle\begin{array}{l}H\\NH_2\end{array}\right. + \begin{array}{l}OC\left\langle\begin{array}{l}COOH\\CH_3\end{array}\right.\\HCO.R\end{array}$$
$$= C_6H_4\left\langle\begin{array}{l}C(COOH){:}CH\\\qquad\quad|\\\qquad N{:}C.R\end{array}\right. + 2H_2O + H_2$$

(Böttinger, A. 191, 321; Döbner, A. 242, 270); quinoline-4′-carboxylic (cinchonic) acid also being obtained by warming isatin with acetone and aqueous caustic soda:



$$C_6H_4\left\langle\begin{array}{l}CO.COOH\\NH_2\end{array}\right. + \begin{array}{l}CH_3\\|\\CO.CH_3\end{array}$$
$$= C_6H_4\left\langle\begin{array}{l}C(COOH){:}CH\\\qquad\quad|\\\qquad N{:}C.CH_3\end{array}\right. + 2H_2O$$

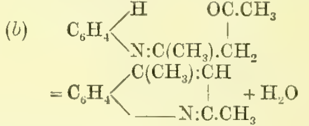
(Pfitzinger, J. pr. [2] 33, 100; 38, 582). For the reaction between aniline and pure acetone, *cf.* Riehm, A. 238, 1.

To prepare quinoline derivatives by this synthetical method, the amine is mixed with twice its weight of fuming hydrochloric acid, and the requisite quantity of aldehyde added gradually, rise of temperature being checked by cooling with water. When β-hydroxyketones are employed, however, it is necessary to bring about the aldol condensation in the first instance by saturating the mixture of ketone and aldehyde with gaseous hydrogen chloride, and allowing the product to stand for some time; the product is then added gradually to the mixture of aniline and hydrochloric acid as just described. After visible reaction ceases in the cold, the product is heated for many hours on a water-bath, digested with water, and the filtrate rendered alkaline by aqueous caustic soda, the precipitated base being subsequently freed from secondary amines by treatment in dilute hydrochloric acid solution with nitrite, and purified either by fractional distillation or by conversion into the sparingly soluble crystalline picrate (*cf.* Harz, B. 18, 3384; v. Miller and Kinkelin, B. 19, 527; Schultz, B. 16, 2600; 17, 1965; Actieng. für Anilinfab., Germ. Pat. 28217 of June 20, 1883; Beyer, J. pr. [2] 33, 401; Reed, J. pr. [2] 35, 299; Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 35133 of July 14, 1885, expired Nov. 1886).

(2) In Döbner and v. Miller's reaction (*supra*) β-hydroxyaldehydes or β-hydroxyketones, $R.CH(OH).CH_2.CO.R'$, are employed, and hydrogen is liberated. If the necessity for oxidation of this hydrogen is removed, and water only requires to be eliminated, as when β-diketones, $R.CO.CH_2.CO.R'$, are employed, the course of the reaction and the yield are improved. The reaction is brought about by heating together molecular proportions of the amine and diketone to form an anilide, which is subsequently warmed for some hours with concentrated hydrochloric acid:

(*a*) $CH_3.CO.CH_2.CO.CH_3 + C_6H_5.NH_2$
$= CH_3.CO.CH_2.C(N.C_6H_5).CH_3$

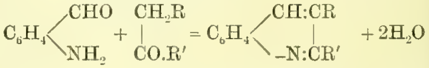
(*b*)



$$C_6H_4\left\langle\begin{array}{l}H\qquad\qquad OC.CH_3\\\qquad\qquad\quad\ |\\N{:}C(CH_3).CH_2\end{array}\right.$$
$$= C_6H_4\left\langle\begin{array}{l}C(CH_3){:}CH\\\qquad\quad|\\\qquad N{:}C.CH_3\end{array}\right. + H_2O$$

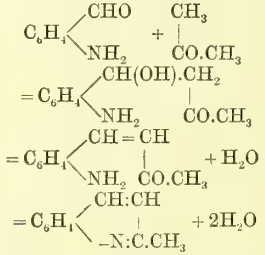
(Beyer, B. 20, 1770; Combes, C. R. 106, 142; 108, 1252).

(3) Hydrogen, again, is not eliminated in the formation of quinoline derivatives by the condensation of orthamidobenzaldehyde with aldehydes, ketones, and similar compounds, and it is on this account, no doubt, that the reaction ensues with such readiness, the reacting substances requiring only to be dissolved in water or aqueous alcohol, and warmed with a few drops of dilute aqueous caustic soda. This reaction, which is due to Friedländer, may be represented by the following equation:



$$C_6H_4\left\langle\begin{array}{l}CHO\\NH_2\end{array}\right. + \begin{array}{l}CH_2R\\|\\CO.R'\end{array} = C_6H_4\left\langle\begin{array}{l}CH{:}CR\\\qquad|\\N{:}CR'\end{array}\right. + 2H_2O$$

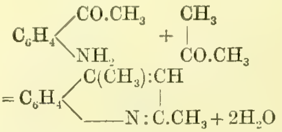
where R and R′ may be hydrogen or alkyl radicles; in all probability aldol condensation ensues in the first instance, water being subsequently eliminated in two stages, with the formation successively of an unsaturated aldehyde or ketone, and finally of a quinoline derivative, thus:



$$C_6H_4\left\langle\begin{array}{l}CHO\\NH_2\end{array}\right. + \begin{array}{l}CH_3\\|\\CO.CH_3\end{array}$$
$$= C_6H_4\left\langle\begin{array}{l}CH(OH).CH_2\\\qquad\qquad|\\NH_2\quad\ \ CO.CH_3\end{array}\right.$$
$$= C_6H_4\left\langle\begin{array}{l}CH{=}CH\\\qquad|\\NH_2\ CO.CH_3\end{array}\right. + H_2O$$
$$= C_6H_4\left\langle\begin{array}{l}CH{:}CH\\\qquad|\\N{:}C.CH_3\end{array}\right. + 2H_2O$$

(Friedländer, B. 15, 2574; Friedländer and Gohring, B. 16, 1835; 17, 456).

Orthamidoacetophenone and orthamidobenzophenone react in certain cases with methyl ketones under like conditions, yielding derivatives of 4′-methyl- or 4′-phenyl-quinoline, thus:



$$C_6H_4\left\langle\begin{array}{l}CO.CH_3\\NH_2\end{array}\right. + \begin{array}{l}CH_3\\|\\CO.CH_3\end{array}$$
$$= C_6H_4\left\langle\begin{array}{l}C(CH_3){:}CH\\\qquad\quad|\\\qquad N{:}C.CH_3\end{array}\right. + 2H_2O$$

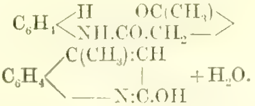
(Geigy and Koenigs, B. 18, 2406; O. Fischer, B. 19, 1037).

(iii.) *Methods which give rise to the production of hydroxyquinolines containing hydroxyl in the 'pyridine-ring.'*

The direct introduction of hydroxyl into the 'pyridine-ring' of quinoline has been accomplished only in a few cases, such as the formation of carbostyril (2′-hydroxyquinoline) by the action of hypochlorous acid on quinoline (Einhorn and Lauch, B. 19, 53; Erlenmeyer and Rosenhek, B. 18, 3295; 19, 489), and therefore synthetical methods must be employed, and of these those with β-ketonic acids and primary amines are the most important.

Ethyl acetoacetate reacts with aniline in two distinct ways, yielding the anilide $C_6H_5NH.CO.CH_2.CO.CH_3$ at temperatures between 110° and 150°, and ethyl β-phenylamidocrotonate, $C_6H_5NH.C(CH_3):CH.COOEt$, at temperatures below 100° (Knorr, A. 236, 73). Both classes of compounds yield quinoline derivatives, the anilide, according to Knorr, forming 2′-hydroxy-4′-methylquinoline, the amidocrotonate, according to Conrad and Limpach, 4′-hydroxy-2′-methylquinoline.

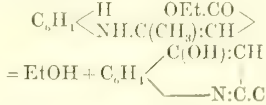
(*a*) In Knorr's reaction molecular proportions of ethyl acetoacetate and aniline are heated under pressure for many hours at 120–150° to form the anilide. The product is then freed from alcohol, dissolved in concentrated sulphuric acid to bring about the condensation to the carbostyril derivative, and, either after standing for some time or warming in a water-bath stirred into water, and the hydroxyquinoline precipitated by neutralisation with aqueous caustic soda. The method gives good yields (Knorr, A. 236, 75, 83; Germ. Pat. 26428 of July 22, 1883). The reaction may be represented thus:



$$C_6H_4\left\langle\begin{matrix}H & OC(CH_3)\\ NH.CO.CH_2 & —\end{matrix}\right\rangle = C_6H_4\left\langle\begin{matrix}C(CH_3):CH\\ |\\ ——N:C.OH\end{matrix}\right. + H_2O.$$

Substituted anilines, homologues of aniline or mono-alkyl derivatives of ethyl acetoacetate, can be employed in place of aniline and ethyl acetoacetate (Knorr, A. 245, 358); secondary anilines, such as methylaniline and its homologues, however, react with ethyl acetoacetate forming lepidone-(2′-ketotetrahydroquinoline-) derivatives (Knorr, A. 236, 106; Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 32281 of Dec. 13, 1884).

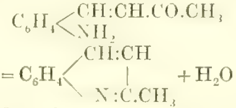
(*b*) The β-amidocrotonate required for the Conrad and Limpach synthesis is prepared by allowing a mixture in molecular proportions of ethyl acetoacetate and the primary aromatic amine (aniline or its homologues) to remain in the cold for a considerable time, or more rapidly by warming carefully on a water-bath. The resulting compound, after dehydration, is converted into the hydroxyquinoline by rapidly heating to 240–250°. Ethyl alcohol, acetone, and the corresponding carbanilide distil over, and the residue is boiled out with water or dilute acid to extract the quinoline derivative, which is precipitated from the acid solution by sodium carbonate or ammonia, and purified by crystallisation from hot water. The residue, insoluble in water, contains the lutidonecarboxylic acid which is always formed as subsidiary product in the condensation. The reaction, so far as the production of the hydroxyquinoline is concerned, may be expressed thus:



$$C_6H_4\left\langle\begin{matrix}H & OEt.CO\\ NH.C(CH_3):CH\end{matrix}\right\rangle = EtOH + C_6H_4\left\langle\begin{matrix}C(OH):CH\\ |\\ ——N:C.CH_3.\end{matrix}\right.$$

The yields are only moderate, ranging from 25–40 p.c. of the theoretical (Conrad and Limpach, B. 20, 947; 21, 523, 1649, 1968; Germ. Pat. 42276 of March 14, 1887; Knorr, B. 20, 1397).

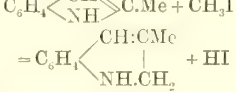
(iv.) In addition to these methods others have been described which, on account of their more limited application, can only find mention here. Baeyer has shown that derivatives of orthamidopropylbenzene containing oxygen in the β- position, either in the ketonic form or as hydroxyl, undergo condensation frequently at the moment of formation with the production of 2′-quinoline derivatives, thus:



$$C_6H_4\left\langle\begin{matrix}CH:CH.CO.CH_3\\ NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH:CH\\ |\\ N:C.CH_3\end{matrix}\right. + H_2O$$

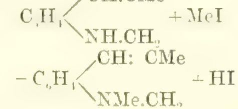
(Baeyer and Jackson, B. 13, 115; Friedländer and Weinberg, B. 15, 1422; Drewsen, B. 16, 1953; Einhorn, B. 17, 2011). Just has obtained derivatives of 4′-hydroxy-2′-phenylquinoline-3′-carboxylic acids by the interaction of benzanilidimido-chloride or its homologues with ethyl sodiomalonate (B. 18, 2632; 19, 979, 1462, 1541; Germ. Pat. 33497 of Feb. 21, 1885, expired July 1890); and E. Fischer has found that alkyl derivatives of indole are converted into 1′:3′-alkyl derivatives of dihydroquinoline by heating with an alkyl iodide and the corresponding alcohol at 100° for 15–20 hours.

(*a*)



$$C_6H_4\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle C.Me + CH_3I = C_6H_4\left\langle\begin{matrix}CH:CMe\\ |\\ NH.CH_2\end{matrix}\right. + HI$$

(*b*)



$$C_6H_4\left\langle\begin{matrix}CH:CMe\\ \\ NH.CH_2\end{matrix}\right. + MeI = C_6H_4\left\langle\begin{matrix}CH:CMe\\ \\ NMe.CH_2\end{matrix}\right. + HI$$

(Fischer and Steche, B. 20, 818, 2200; A. 242, 353).[1] For the preparation of chloroquinolines by the condensation of malonanilic acid, $C_6H_5NH.CO.CH_2.COOH$, and its homologues with phosphorus pentachloride *cf.* Rugheimer and Hoffmann, B. 17, 737; Rugheimer and Schramm, B. 20, 1236.

ALKYL DERIVATIVES.

(i.) **Quinaldine.** 2′-*Methylquinoline.*

Formation.— Quinaldine occurs in coal-tar quinoline to the extent of about 25 p.c. (Jacobsen and Reimer, B. 16, 1084; Jacobsen, Germ. Pat. 23967). It is obtained synthetically by warming a mixture of aniline and aldol with concentrated hydrochloric acid (Döbner and Miller, B. 16, 2465); by heating crotonic aldehyde with aniline, nitrobenzene, and sulphuric acid (Skraup, B. 15, 897); by warming orthamidobenzaldehyde and acetone in aqueous solution with a small quantity of caustic soda (Friedländer and Gohring, B. 16, 1835); by heating acetonyl-quinoline with concentrated hydrochloric acid at 170° (O. Fischer and Kuzel, B. 16, 165), by reducing orthonitrobenzylidene-acetone with stannous chloride (Drewsen, B. 16, 1954; Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 22138 of July 25, 1882, expired Dec. 1886; Eng. Pat. 3541 of 1882), and is best prepared by warming a mixture of $1\frac{1}{2}$ parts of paraldehyde, one part of aniline, and two parts of strong hydrochloric acid for some hours on a water-bath (Döbner and Miller, *l.c.*, Chem. Fab. auf Actien. (vorm. E. Schering), Germ. Pat. 24317 of Aug. 19, 1882, Eng. Pat. 956 of 1883; Actieng. für Anilinfab., Germ. Pat. 28217 of June 20, 1883; Eng. Pat. 4207 of 1883 (*v. supra*).

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[1] This reaction, which at first sight appears to correspond with Ciamician's synthesis of pyridine-from pyrrole-derivatives (B. 14, 1154; 15, 1173), differs, however, in that the entering carbon atom assumes an α- and not a β- position to the nitrogen atom. As Magnanini has shown, the Ciamician reaction can be extended to indoles, methylketole yielding 3′-chloroquinaldine on treatment with chloroform and sodium ethylate (B. 20, 2609; G. 19, 569).

Properties.—It is a colourless, strongly refractive oil, which has a slight quinoline-like odour, and boils at 238-239° under 716 mm. pressure (Döbner and Miller, B. 14, 2814); at 244–245° under 750 mm. pressure (Hoogewerff and van Dorp, Rec. trav. chim. 3, 344). The salts, as a rule are readily soluble in water; the *chromate* is characterised by crystallising in yellowish-red needles sparingly soluble in cold water.

Quinaldine when heated with phthalic anhydride and zinc chloride is converted into *quinophthalone* (*v. infra*). Condensation compounds are also formed with aldehydes, and of these the compound with chloral is converted by treatment with alkalis and subsequent oxidation with potassium permanganate into *2′-quinoline-aldehyde* (Miller and Spady, B. 18, 3404; 19, 130; Einhorn, B. 18, 3467; Farb. vorm. Meister, Lucius & Brüning, Germ. Pat. 36964 of Dec. 29, 1885; expired May 1890). On oxidation with concentrated nitric acid it yields *nitroquinoline-2′-carboxylic acid* (Döbner and Miller, B. 15, 3076); with potassium permanganate it forms *acetylanthranilic acid* and oxalic acid (*ibid.*, B. 15, 3077), and with chromic anhydride and sulphuric acid it yields *quinaldinic* (quinoline-2′-carboxylic) acid (Döbner and Miller, B. 16, 2472). Treatment with tin and hydrochloric acid converts it into the *tetrahydro-* derivative (Döbner and Miller, B. 16, 2467). When dissolved in an equivalent quantity of concentrated nitric acid, and the solution gradually added to a mixture of 6 parts of fuming nitric acid and 6 parts of concentrated sulphuric acid, a mixture of 39 p.c. of *ortho-* and 61 p.c. of *meta-nitroquinaldine* is obtained (Döbner and Miller, B. 17, 1699; Gerdeissen, B. 22, 245). On sulphonation with fuming sulphuric acid at 100° quinaldine yields a mixture of the *ortho-*, *meta-* and *para- monosulphonic acids* (Döbner and Miller, B. 17, 1703; Chem. Fab. auf Actien. (vorm. E. Schering), *l.c.*, Germ. Pat. 29819 of Oct. 2, 1883; Richard, B. 23, 3488).

(ii.) **Lepidine.** *4′-Methylquinoline.*

Formation.—Lepidine occurs in the product formed by distilling cinchonine with caustic potash (G. Williams, Trans. R. S. Edin. [3] 21, 377; *cf.* Oechsner, Bl. 38, 546), and has been prepared synthetically by saturating a mixture of methylal and acetone with gaseous hydrogen chloride, adding aniline, and heating with concentrated hydrochloric acid (Beyer, J. pr. [2] 33, 418; Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 35133 of July 14, 1885; expired Nov. 1886; *v. supra*).

Preparation.—The fraction, b.p. = 250–260°, of the product obtained by distilling cinchonine with caustic potash is dissolved in 3–4 parts of warm alcohol, and converted into acid sulphate by the addition of 2 parts of sulphuric acid (sp.gr. = 1·53). The crystalline sulphate which separates is then decomposed by potash (Hoogewerff and van Dorp, Rec. trav. chim. 2, 1).

Properties.—Lepidine is an oil, with the odour of quinoline. It boils at 265·5° under 746·7 mm. pressure, has a sp.gr. = 1·0862 at 20° (Krakau), and is miscible in all proportions with alcohol, ether, benzene, &c. On oxidation with chromic acid mixture it is slowly converted into *cinchoninic* (quinoline-4′-carboxylic) acid.

HYDROXY- DERIVATIVES.

Hydroxy- derivatives of quinoline, quinaldine, and lepidine are obtained by the synthetical methods already described (*v. supra*), but mention can only be made of three of the isomeric hydroxyquinolines. These hydroxy- derivatives resemble the phenols in properties, forming with caustic alkalis salts which are decomposed by carbon dioxide; and in the case of ortho- and parahydroxyquinoline yielding yellow, red, or brown azo- dyes on treatment with diazotised bases (O. Fischer and Renouf, B. 17, 1642). On reduction with tin and hydrochloric acid the corresponding *tetrahydro-* derivatives are produced in the case of those compounds which contain the OH radicle in the 'benzene-ring'; those which contain the radicle in the 'pyridine-ring,' however, are not reduced under these conditions, but on treatment in boiling alcoholic solution with sodium eliminate the hydroxyl with the formation of *tetrahydro-* derivatives of quinoline or its homologues.

(i.) **Orthohydroxyquinoline.** *Quinophenol* $C_9H_6N(OH)$.

Preparation.—Orthohydroxyquinoline is prepared either by heating a mixture of orthamidophenol and orthonitrophenol with glycerol and sulphuric acid at 130–140° (Skraup, M. 3, 536; Germ. Pat. 14976 of Feb. 16, 1881; Eng. Pat. 678 of 1881), or by fusing quinolineorthosulphonic acid with 2–3 times its weight of caustic soda (Bedall and O. Fischer, B. 14, 443, 1366).

Properties.—It crystallises from dilute alcohol in long, lustrous, prismatic needles, melts at 76°, boils at 226·6° under 752 mm. pressure (Skraup), is volatile with steam, and is sparingly soluble in water and ether, readily soluble in alcohol and benzene. Ferric chloride added to its solution gives an intense green colouration, which on addition of sodium carbonate becomes darker with the separation of a greenish-black precipitate. Like the orthohydroxytoluquinolines, quinophenol gives intense yellow and grey colours with aluminium and iron mordants respectively (Nölting and Trautmann, B. 23, 3660). The *methoxy-* derivative, *orthoquinanisoïl*, obtained either by methylating orthohydroxyquinoline (Bedall and O. Fischer, B. 14, 2570) or by the Skraup reaction from orthanisidine (Skraup, M. 3, 540), boils at 265°–266°, and on reduction with tin and hydrochloric acid is converted into the *tetrahydro-* derivative.

Derivatives.—Orthohydroxytetrahydroquinoline, obtained by reduction of orthohydroxyquinoline with tin and hydrochloric acid and subsequent decomposition of the resulting stannochloride with sulphuretted hydrogen, crystallises in colourless needles, melts at 121–122°, is not volatile with steam, and dissolves fairly readily in hot water (Bedall and O. Fischer, B. 14, 1368).

Kairine. *Orthohydroxytetrahydro-*1′*-methylquinoline* $OH.C_9H_9.NMe$.

Preparation. — Molecular proportions of orthohydroxytetrahydroquinoline and methyl iodide are carefully mixed together, and when the vigorous reaction has ceased the product is gently heated in a reflux apparatus until all odour of methyl iodide has disappeared, then dissolved in water, precipitated by caustic soda, and the separated base rapidly filtered, washed with water, and crystallised from ether or benzene (O. Fischer, B. 16, 714; Germ. Pat. 21150 of March 1, 1882; expired July 1884; Eng. Pat. 3044 of 1882).

Properties.—It crystallises from ether in rhombic tables, from alcohol in prismatic forms, melts at 114°, and is sparingly soluble in water, readily in warm alcohol, benzene, or aqueous caustic potash. In alcoholic solution it gives with ferric chloride a deep-brown colouration, and in dilute sulphuric acid solution it yields with sodium nitrite a reddish-yellow colouring matter. The *hydrochloride*, $C_{10}H_{13}NO,HCl + H_2O$, crystallises in colourless, lustrous, monoclinic forms, dissolves readily in water, and was at one time employed as a febrifuge, under the name kairine.

Orthohydroxytetrahydro-1′-ethylquinoline $OH.C_9H_9.NEt$, obtained by ethylating orthohydroxytetrahydroquinoline, crystallises from ether in monoclinic tables or scales (O. Fischer, B. 16, 717; O. Fischer and Renouf, B. 17, 756), melts at 76°, and is sparingly soluble in water, readily in alcohol, benzene, &c. The *hydrochloride*, $C_{11}H_{15}NO,HCl$, crystallises in rhombic prisms or needles, is readily soluble in water, has a cooling taste, which afterwards becomes bitter, and was employed as an antipyretic, under the name kairine-A.

Kairocoll, $C_{11}H_{11}NO_2$, prepared by the action of chloracetic acid in aqueous solution on orthohydroxytetrahydroquinoline at 100°, crystallises in long slender needles, melts at 66°, and is sparingly soluble in water, readily in alcohol and ether (O. Fischer, B. 16, 718).

(ii.) **Parahydroxyquinoline.**

Preparation.—Parahydroxyquinoline is prepared by heating a mixture of paramidophenol and paranitrophenol with glycerol and sulphuric acid in the ordinary way (Skraup, M. 3, 545; Germ. Pat. 14976 of Feb. 16, 1881; Eng. Pat. 678 of 1881), and by fusing quinolineparasulphonic acid (obtained either by the Skraup method from sulphanilic acid (Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 26430 of Aug. 3, 1883), or by heating quinoline with seven times its weight of concentrated sulphuric acid of 66°Bé. at 275°–280° for 24 hours (Bad. Anilin- & Sodafab., Germ. Pat. 40901 of March 5, 1887)) with 2–3 times its weight of caustic soda (Farbw. vorm. Meister, Lucius & Brüning, *l.c.*; O. Fischer and Willmack, B. 17, 440; Happ, B. 17, 193).

Properties.—It crystallises from alcohol in small prisms, melts at 193°, boils above 360°, does not volatilise with steam, and is very sparingly soluble in cold water and ether, more soluble in alcohol, and readily soluble in acids and alkalis. In dilute alcoholic solution it gives with ferric chloride a pale-yellow colour.

Derivatives. — Paramethoxyquinoline, *paraquinanisoïl*, $C_9H_6N.OMe$, is obtained either by methylating parahydroxyquinoline (Skraup, M. 3, 544), or by heating a mixture of paranisidine and paranitranisoïl with glycerol and sulphuric acid at 140–150° (Skraup, M. 6, 762; Bad. Anilin- & Sodafab., Germ. Pat. 28324 of Nov. 11, 1883). It is an oil which boils with slight decomposition at 304–305° under 740 mm. pressure, but without decomposition at 193° under 50 mm. pressure, and has a sp.gr. =1·1542 at 20°. The aqueous solutions of its salts show a blue fluorescence, and on treatment with chlorine-water and ammonia give a green colouration, and subsequently a green precipitate, thus resembling quinine salts. It gives no colouration with ferric chloride.

Thalline. *Tetrahydroparamethoxyquinoline*, *Tetrahydroparaquinanisoïl*, $C_9H_{10}N.OMe$.

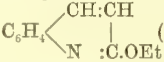
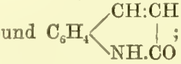
Preparation.—A mixture of 4 parts of granulated tin, 15 parts of hydrochloric acid of sp.gr. =1·14, and 1 part of paraquinanisoïl hydrochloride is warmed for 8–10 hours on a water-bath. On cooling, the sparingly soluble crystalline stannochloride separates, and is decomposed by treatment with zinc, which converts it into the zincochloride, a minimum of water being employed so that the zinc salt will just dissolve at the boiling-point. The zincochloride is finally decomposed by excess of alkali, and the base, which separates as an oil but afterwards crystallises, is purified by crystallisation from alcohol (Bad. Anilin- & Sodafab., Germ. Pat. 30426 of June 18, 1884). The stannochloride may also be decomposed by sulphuretted hydrogen (Skraup, M. 6, 767).

Properties.—Thalline crystallises from alcohol in thick rhombic prisms, melts at 42–43°, boils at 283° under 735 mm. pressure, and is very sparingly soluble in cold water, readily soluble in alcohol and benzene. The aqueous solutions of its salts are coloured an intense green by ferric chloride, chlorine water, and other oxidising agents. Thalline, as sulphate or tartrate, was at one time employed as an antipyretic. The *sulphate* $(C_{10}H_{13}NO_2)_2,H_2SO_4 + 2H_2O$, crystallises from dilute alcohol in long needles, dissolves in 5 parts of water at the ordinary temperature, and is very sparingly soluble in absolute alcohol; the *tartrate*, $B.C_4H_6O_6$, forms rhombic tables, and dissolves in 10 parts of water at 15° (Flückiger, J. 1886, 931).

(iii.) **Carbostyril** 2′*Hydroxyquinoline.*

Formation.—Carbostyril has been prepared by reducing ethyl orthonitrocinnamate with alcoholic ammonium sulphide (Friedländer and

Ostermaier, B. 14, 1916; *cf.* Chiozza, A. 83, 118), by heating orthamidocinnamic acid with hydrochloric acid in a reflux apparatus for some time (Tiemann and Oppermann, B. 13, 2070; *cf.* Baeyer and Jackson, B. 13, 115), by heating 4′-hydroxydihydrocarbostyril (Einhorn, B. 17, 2012), by heating quinoline with an excess of bleaching-powder solution until reaction ceases (Erlenmeyer and Rosenhek, B. 18, 3295; Einhorn and Lauch, B. 19, 53), and by boiling orthamidocinnamic acid for some time with 5 parts of 50 p.c. sulphuric acid (Feer and Koenigs, B. 18, 2395).

Properties.—It crystallises from alcohol in large prisms, from a 1 p.c. aqueous solution with 1 mol. prop. H_2O in longer and very slender needles, melts at 199°, and is scarcely soluble in cold water, readily in hot water, alcohol, and ether. On oxidation with potassium permanganate in alkaline solution it yields *isatin* and *kynuric* or *carbostyrilic acid*, $COOH.C_6H_4.NH.C(OH)_2.COOH$ (Friedländer and Ostermaier, B. 15, 332). Acid reducing agents do not act upon it, but on treatment in boiling alcoholic solution with sodium it yields *tetrahydroquinoline* (Knorr and Klotz, B. 19, 3302). In many of its reactions, carbostyril has the properties of a phenol; thus it forms salts with caustic alkalis and its silver salt on digestion with ethyl iodide gives the ether  $C_6H_4\left<\begin{array}{l}CH{:}CH\\ \quad\ |\\ N\ \ {:}C.OEt\end{array}\right.$ (Friedländer and Weinberg, B. 15, 1422), in others, however, it has the properties of a keto- compound  $C_6H_4\left<\begin{array}{l}CH{:}CH\\ \qquad\ |\\ NH.CO\end{array}\right.$; thus on treatment in alcoholic solution with sodium ethylate and ethyl iodide it yields 1′-ethylpseudocarbostyril or 1′-ethyl-2′-ketodihydroquinoline (Friedländer and Weinberg, B. 18, 1528; Friedländer and Müller, B. 20, 2009).

QUINOLINE COLOURING MATTERS.

The dyes obtained from quinoline derivatives are few in number, and, with the exception of alizarin-blue, have no commercial value on account either of their cost or the fugitive nature of the colours. In addition to the colouring matters mentioned below, alizarin-blue (*v.* ALIZARIN AND ALLIED COLOURING MATTERS) and chrysaniline (*q.v.*) are quinoline dyes, but have already been described.

(i.) **Flavaniline** 2′-*Paramidophenyl*-4′-*methylquinoline* $C_{16}H_{14}N_2$ (Besthorn and O. Fischer, B. 16, 68; O. Fischer and Taüber, B. 17, 2928.)

Preparation.—Flavaniline is obtained by the action of zinc chloride on acetanilide or acetylamidobenzoic acid at 250–270° for many hours, and separated by extracting the product with dilute hydrochloric acid and adding salt and some sodium acetate to the solution; the yield, however, is not good (O. Fischer and Rudolph, B. 15, 1500; Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 19766 of Dec. 10, 1881; 21682 of April 6, 1882, exp. April 1885; Eng. Pat. 5427 of 1881). It has also been prepared by heating aniline hydrocloride with acetic anhydride at 180–200° for 12 hours (Baum, Germ. Pat. 27948 of July 3, 1883, expired Nov. 1886), by heating acetanilide hydrochloride at 280° for 6 hours (Nölting and Weingärtner, B. 18, 1341), and by heating either orthamidoacetophenone at 250°, or a mixture of ortho- and para-amidoacetophenone at 100°, with zinc chloride (O. Fischer, B. 19, 1037), a fair yield being obtained in the last case.

Properties. — Flavaniline crystallises from benzene in long needles, melts at 97° and is slightly soluble in water, readily soluble in alcohol. It forms two series of salts, and its orange-red, microcrystalline *hydrochloride* $C_{16}H_{14}N_2,HCl$ has been employed as a bright-yellow dye for silk and wool (Köchlin, D. P. J. 253, 86). It dissolves in concentrated sulphuric acid forming a colourless fluorescent solution, but is sulphonated by anhydrosulphuric acid with the formation of Flavaniline-S., a greenish-yellow dye for wool. When diazotised, flavaniline is converted into *flavenol* $C_{16}H_{13}NO$ (m.p. = 238°), which on distillation with zinc-dust is reduced to *flavoline.*

Derivative. — Flavoline (2′-*phenyl*-4′-*methylquinoline*) $C_{16}H_{13}N$, obtained by reduction of flavenol, has been prepared synthetically by heating a solution of orthamidoacetophenone and acetophenone in aqueous alcohol with 10 p.c. aqueous caustic soda at 100° (O. Fischer, B. 19, 1037). It crystallises in white scales or thick tables, melts at 64–65°, distils above 300° without decomposition, and on nitration and subsequent reduction is converted into *flavaniline.*

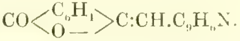
(ii.) **Cyanine** or **Quinoline-blue** $C_{29}N_{35}N_2I$. Cyanine was prepared by G. Williams (Trans. R. S. Edin. 31 (1856), 377) by the action of alkalis on the product obtained by heating cinchonine-quinoline with amyl iodide (C. N. 2, 219) and examined later by Hofmann (Pr. 12, 410), Nadler and Merz (J. pr. 100, 129) and Spalteholz (B. 16, 1847). According to Hoogewerff and van Dorp (Rec. trav. chim. 2, 28, 41, 317; 3, 337), colouring matters of the cyanine class are formed by the action of caustic potash upon molecular proportions of quinoline and lepidine alkyl iodides, thus:

$$C_9H_7N,XI + C_{10}H_9N,YI = C_{19}H_{13}N_2,XYI + HI + H_2.$$

Preparation.—The amyl derivatives of quinoline and lepidine are first prepared by digesting the bases with amyl iodide in alcoholic solution on a water-bath. A solution of 1 part of amylquinoline iodide (m.p. = 184–185°) and 2 parts of amyllepidine iodide (m.p. = 158–160°) in 20 parts of warm alcohol is treated with the requisite amount of caustic potash, the alcohol removed by distillation, and the dye-stuff either extracted from the residue by acetone, or the resinous matters dissolved out by benzene, in which cyanine is insoluble. A third method of separation, precipitation of the very sparingly soluble periodide $C_{29}H_{35}N_2I + I_2$ (m.p. = 187–189°), by addition of an alcoholic solution of iodine to the alcoholic solution of the product, and subsequent conversion into cyanine by treatment with alkali, can also be employed. The yield amounts to about 50 p.c. of the amyllepidine used (Hoogewerff and van Dorp, Rec. trav. chim. 3, 337).

Properties. — Cyanine crystallises in long needles with $1\frac{1}{2}$ H_2O (*ibid.*), and from alcohol by slow evaporation in cantharides-green, monoclinic (Arzruni, Rec. trav. chim. 3, 354) tables, melts at 100° to a bronze-coloured liquid, and is insoluble in water and ether, but soluble in alcohol. It combines with 1 and 2 mol. props. of monobasic acids forming salts, which are respectively blue and colourless. Cyanine dyes silk a beautiful blue, which by lamp-light appears lilac, but the colours are very fugitive. It finds a limited use in photography (*v. Quinoline-red, infra*).

Other cyanines, such as dimethylcyanine iodide $C_{21}H_{19}N_2I$ and the diethylcyanine iodides $C_{23}H_{23}N_2I$ from lepidine and from quinaldine have been described (Spalteholz, *l.c.*; Hoogewerff and van Dorp, Rec. trav. chim. 2, 317; 3, 337).

(iii.) **Quinophthalone** *Spirit-soluble quinoline-yellow*  $CO\left\langle\begin{array}{l}C_6H_4\\ O\text{—}\end{array}\right\rangle C:CH.C_9H_6N$.

Preparation.—Molecular proportions of quinaldine (10 parts) and phthalic anhydride (12 parts) are fused with zinc chloride (12 parts) at 200–210° for 5–6 hours. The melt is boiled out with dilute hydrochloric acid to extract zinc chloride, phthalic acid and unattacked base, and the insoluble residue filtered, ground, and dried (Jacobsen and Reimer, B. 16, 513, 1082, 2602; Germ. Pat. 23188 of Nov. 4, 1882; 25144 of April 18, 1883; Eng. Pat. 1362 of 1883; Traub, B. 16, 297, 878).

Properties.—Quinophthalone crystallises from alcohol in slender, golden-yellow needles, melts at 234–235°, is insoluble in water, sparingly soluble in boiling alcohol, readily soluble in acetic acid and chloroform. When heated with excess of alcoholic ammonia at 200° for 40 hours it is converted into a basic yellow colouring matter quinophthalin $C_{18}H_{12}N_2O$ (Farbw. vorm. Meister, Lucius & Brüning, Germ. Pat. 27785 of Nov. 20, 1883, expired April 1891). Concentrated sulphuric acid dissolves it, forming a yellow solution, but anhydrosulphuric acid converts it into

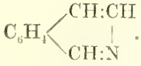
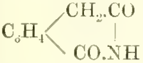
Quinoline-yellow, which consists of a mixture of quinophthalonemono- and di- sulphonic acids as sodium salts.

Preparation.—Quinoline-yellow is obtained by dissolving quinophthalone in 3–3·5 parts of 'fuming' sulphuric acid in the cold, the product being converted into calcium salt, and thence into sodium salt in the usual way.

It is a yellow powder, which dissolves readily in water and dyes wool a fast greenish-yellow in an acid bath.

(iv.) **Quinoline-green** has been prepared by the action of phosphorus oxychloride (0·9 part) on a mixture of quinoline (2 parts), and tetramethyldiamidobenzophenone (1·4 parts). The zinc chloride, obtained by precipitating the aqueous solution of the product with salt and zinc chloride, gives bluish-green shades on animal fibres, and on cotton mordanted with tannin, but does not appear to have been employed as a dye-stuff (Bad. Anilin- & Sodafab., Germ. Pat. 27789 of Dec. 18, 1883).

(v.) In addition to these colouring matters, a violet dye for silk, wool, and cotton has been obtained by heating quinoline (50 parts) with rosaniline (10 parts) and benzoic acid (1 part) at 130–140°, until the evolution of ammonia ceases (Bad. Anilin- & Sodafab., Germ. Pat. 49008, of April 11, 1889).

Isoquinoline  $C_6H_4\left\langle\begin{array}{l}CH:CH\\ \quad\;|\\ CH:N\end{array}\right.$. Isoquinoline is present in coal-tar quinoline (Hoogewerff and van Dorp, Rec. trav. chim. 4, 125, 285; 5, 305; *cf.* Dewar, Pr. 30, 167). It has been prepared synthetically from homo-orthophthalimide  $C_6H_4\left\langle\begin{array}{l}CH_2.CO\\ \qquad|\\ \;CO.NH\end{array}\right.$ by distillation with zinc-dust in a current of hydrogen (Le Blanc, B. 21, 2299), and from α-β-dichloroisoquinoline (obtained, together with α-chloro-β-hydroxyisoquinoline, by the action of phosphorus oxychloride on homo-orthophthalimide at 150–170°) by reduction with hydriodic acid (sp.gr. = 1·96) at 230° (Gabriel, B. 19, 2361).

Preparation.—The acid sulphates of quinoline and quinaldine are more soluble in alcohol than the isoquinoline salt. Coal-tar quinoline is therefore dissolved in twice its weight of 95–96 p.c. alcohol, one mol. prop. of sulphuric acid added, and the whole allowed to stand for some time in the cold. The separated crystalline sulphates of quinoline and isoquinoline are decomposed by caustic potash, and the mixed bases fractionated between 230–236° and 236–243°. The latter fraction is again converted into acid sulphate, and this is repeatedly crystallised from twice its weight of 88 p.c. alcohol until its melting-point rises to 205° (Hoogewerff and van Dorp, *l.c.*).

Properties. — Isoquinoline crystallises in tables, melts at 22°, boils at 236·5° (Gabriel), at 240·5° (therm. in vapour) under 763 mm. pressure (Hoogewerff and van Dorp), has a quinoline-like odour, and is volatile with steam. On oxidation with potassium permanganate in alkaline solution, it yields ammonia, *phthalic acid*, *cinchomeronic* (pyridine-3-4-dicarboxylic) *acid*, and traces of oxalic acid (Rec. trav. chim. 4, 285); in neutral solution, however, it is converted into *phthalimide* (Goldschmiedt, M. 9, 676). Isoquinoline possesses considerable interest in view of the fact that among its derivatives are the vegeto-alkaloids papaverine (Goldschmiedt, M. 6, 667), narcotine (Roser, A. 254, 357), hydrastine (Freund and Rosenberg, B. 23, 414), and berberine (W. H. Perkin, jun., C. J. 57, 1006). One colouring matter has been obtained from isoquinoline, namely—

Quinoline-red, *isoquinoline-red* $C_{26}H_{19}N_2Cl$. This dye, which, from its mode of formation, belongs to the malachite-green series, was obtained by E. Jacobsen by the action of benzotrichloride, benzochlorodibromide, or benzal chloride, on a mixture of coal-tar quinoline and zinc chloride (Germ. Pat. 19306 of Feb. 14, 1882, exp. June 1886; 23967 of Dec. 16, 1882, exp. June 1886), and is formed by the interaction of benzotrichloride, isoquinoline, and quinaldine in molecular proportions, either at 150°, or more rapidly in the presence of zinc chloride at 120°.

Preparation.—(1) A mixture of 25 grams of zinc chloride and 100 grams of coal-tar quinoline (b.p. 235–240°) is warmed on a water-bath, and treated with 40 grams of benzotrichloride, added at such a rate that the temperature does not rise beyond 120–130°. The product is then mixed with a litre of milk of lime (containing

100 grams CaO), the unattacked quinoline[1] (about 50 p.c.) separated by steam distillation, and the residue filtered. The clear filtrate, after treatment with 25 c.c. of hydrochloric acid of 21°Bé., gives, on cooling, an almost complete separation of the dyestuff in the crystalline form. The yield amounts to about 10 p.c. of the quinoline actually employed (Zierold, quoted by Hofmann, B. 20, 5).

(2) For photographic purposes a very pure quinoline-red is required, and it is preferable, therefore, to bring about the condensation with pure quinaldine and a material, which, if not pure isoquinoline, contains it in considerable quantity. 10 parts of isoquinoline and 11 parts of quinaldine are heated with 5 parts of zinc chloride at 120–130°, 15 parts of benzotrichloride are gradually added at this temperature, and the melt worked up as before. Tolu- and xyloquinaldines may be employed instead of quinaldine in this reaction (Actieng. für Anilinfab., Germ. Pat. 40420 of Nov. 2, 1886).

Properties.—Quinoline-red forms dark-red, bronze-lustred needles or thin monoclinic prisms, and is almost insoluble in cold water, but readily soluble in hot water and alcohol, forming solutions which are carmine-red by transmitted light, and in reflected light show a marked yellowish-red fluorescence. On reduction with zinc and hydrochloric acid it is quickly decolourised with the formation of a leuco-base; but when heated with alcoholic ammonium sulphide at 200° it yields benzylmercaptan (derived from the group introduced in the form of benzotrichloride) and a new base $C_{19}H_{14}N_2$, which crystallises in plates of golden lustre and melts at 231° (Hofmann, *l.c.*). Quinoline-red dyes wool and silk bright rose, with some indication of yellow fluorescence, and also dyes mordanted cotton, giving, however, non-fluorescent shades; the colours are not fast to light. As a dyestuff it is valueless, but with cyanine it finds a limited employment in the preparation of 'azaline-plates' for photographic purposes (Vogel, Germ. Pat. 39779 of May 16, 1886; *v.* PHOTOGRAPHY).

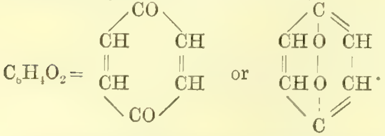
A second quinoline-red is obtained by employing quinoline instead of isoquinoline in the above preparation, but the yield amounts only to 1·5 p.c. No difference has been detected in the chemical behaviour of the two reds, but the solutions of the red prepared from quinoline are crimson, with a slight violet tint; and although the absorption spectrum of both dyes consists of two bands in the green and bluish-green, the bands of quinoline-red are narrower and more intense than those of isoquinoline-red.

W. P. W.

QUINOLINE DYES *v.* QUINOLINE.

QUINOLINIC ACID *v.* BONE OIL.

QUINONE (*kinone*; *Chinon*, Ger.).



Quinone was first obtained, in 1838, by Woskresensky (A. 27, 268) by the oxidation of quinic acid with manganese dioxide and dilute sulphuric acid. It is formed by the oxidation of many para-disubstitution derivatives of benzene, such as *p*-dihydroxybenzene (*quinol, hydroquinone*), *p*-amidophenol, sulphanilic acid, and others. Best prepared by dissolving 1 part of aniline in 8 parts of sulphuric acid diluted with 25 parts of water, and gradually adding to the liquid a concentrated solution of sodium bichromate. The solution is then twice extracted with ether, which on evaporation deposits the quinone (Nietzki, B. 19, 1,468; Seyda, B. 16, 687; *v.* also Schniter, B. 20, 2,283). The quinone may be purified by recrystallisation from light petroleum.—Thin yellow prisms, melting at 115°. Sublimes readily, and is volatile with steam; has a peculiar and penetrating odour; is sparingly soluble in cold water, more readily in hot water, alcohol, and ether. The aqueous solution stains the skin brown. Reducing agents, such as sulphurous acid, stannous chloride, or hydriodic acid, readily convert it into quinol $C_6H_4(OH)_2$ (1, 4); and, as an intermediate stage, quinhydrone $C_{12}H_{10}O_4$ (Wöhler), $C_{18}H_{14}O_6$ (Wichelhaus) is formed, a compound which may also be obtained by the direct union of quinone with quinol. Concentrated nitric acid dissolves it in the cold without decomposing it, but hot nitric acid converts it into picric acid and oxalic acid. It unites with gaseous hydrochloric acid to form chlorquinol $C_6H_3Cl(OH)_2$ (*cf.* following article). With free chlorine it yields chiefly trichlorquinone, whilst potassium chlorate and hydrochloric acid convert it into tetrachlorquinone (*v. infra*). Heated with hydroxylamine hydrochloride it forms *p*-nitrosophenol $C_6H_4O(N.OH)$ and quinone-dihydroxime $C_6H_4(N.OH)_2$. Reacts with primary amines, yielding crystalline compounds; thus with aniline it forms dianilidoquinone $C_6H_2O_2(NH.C_6H_5)_2$.

Tetrachlorquinone (*chloranil*) $C_6Cl_4O_2$, the most important of the halogen substitution derivatives of quinone, was obtained by Erdmann, in 1841, by treating chlorisatin or dichlorisatin with chlorine (A. 48, 309). Formed by the action of potassium chlorate and hydrochloric acid on various benzene compounds, such as aniline, phenol, and salicylic acid. Best prepared from the mixture of phenol-sulphonic acids, obtained by heating phenol with an equal weight of concentrated sulphuric acid on the water-bath. This mixture is dissolved in 20 times its weight of hot water, together with from 2 to 2·5 parts of potassium chlorate, and an excess of strong hydrochloric acid is added. The reaction soon begins; the liquid turns brown, whilst chlorine and its oxides escape, and yellow crystalline laminæ separate on the surface. After standing for 24 hours, steam is blown into the mixture in order to finish the reaction. The yellow crystalline substance is separated by filtration through calico and washed with water. The crude product thus obtained consists of a mixture of trichlorquinone and tetrachlorquinone. To prepare from it pure tetrachlorquinone it is first boiled for some hours with concentrated hydrochloric acid, which converts the trichlorquinone into tetrachlorquinol

$$C_6HCl_3O_2 + HCl = C_6Cl_4(OH)_2,$$

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[1] The recovered quinoline gives practically no quinoline-red on a second treatment with benzotrichloride, since it is almost completely free from isoquinoline and quinaldine.

after which the tetrachlorquinol is oxidised to tetrachlorquinone with nitric acid or chromic acid (Knapp & Schultz, A. 210, 174).—Golden yellow laminæ, which sublime without previous fusion, insoluble in water, sparingly soluble in alcohol, more readily soluble in benzene. Exceedingly stable towards oxidising agents; concentrated nitric acid and aqua-regia are without action on it. Concentrated sulphuric acid does not attack it. Reducing agents, such as sulphurous acid and hydriodic acid, convert it into tetrachlorquinol; and it is even reduced by boiling with concentrated hydrochloric or hydrobromic acid:

$$C_6Cl_4O_2 + 2HCl = C_6Cl_4(OH)_2 + Cl_2.$$

When heated with acetyl chloride to 160–180°, it yields the diacetyl derivative of tetrachlorquinol:

$$C_6Cl_4O_2 + 2C_2H_3OCl = C_6Cl_4(O.C_2H_3O)_2 + Cl_2$$

(Graebe, A. 146, 12). Phosphorus pentachloride at 180° converts it into hexachlorbenzene:

$$C_6Cl_4O_2 + 2PCl_5 = C_6Cl_6 + 2POCl_3 + Cl_2.$$

Ammonia and primary amines react with it, replacing two chlorine atoms by two amido- or substituted amido- groups; thus ammonia yields diamido-dichlorquinone $C_6Cl_2(NH_2)_2O_2$, and aniline dianilido-dichlorquinone $C_6Cl_2(NH.C_6H_5)_2O_2$; these compounds give a blue colouration with cold concentrated sulphuric acid. Caustic potash solution also withdraws two chlorine atoms, forming potassium chloranilate $C_6Cl_2(OK)_2O_2$, which dissolves in water with an intense violet colour.

Tetrachlorquinone oxidises the leuco- compounds of the rosaniline group, such as leucaniline and leucomalachite green, to the corresponding colour-bases (Greiff, B. 12, 1610; Germ. Pat. 11412 of Nov. 11, 1879, expired March 1887). In like manner it may be used to oxidise various bases of the benzene series—such as dimethylaniline, methyldiphenylamine—so as to convert them into colouring matters, which are identical with those obtained from the same bases with other oxidising agents (Germ. Pats. 8251 of June 24, 1879, and 11811 of Nov. 12, 1879; *v.* also B. 12, 1952; 16, 2005, 2904, and 3044; 17, 100). These processes have not proved successful on a large scale. F. R. J.

QUINONES. The quinones are a class of compounds in which two hydrogen atoms, either in the para- or in the ortho- position in a benzenoid hydrocarbon, are replaced by two atoms of oxygen.

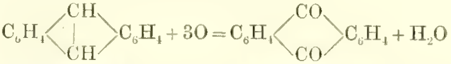
Graebe (A. 146, 1; Z. 1867, 39) regarded the oxygen atoms in the quinones as linked together to form the dyad complex O-O. This accounted for the fact that the two oxygen atoms replace two hydrogen atoms, and also that the two oxygen atoms in tetrachlorquinone may be replaced by two chlorine atoms, instead of by four, when this compound is heated with phosphorus pentachloride:

$$C_6Cl_4(O_2)'' + 2PCl_5 = C_6Cl_6 + 2POCl_3 + Cl_2.$$

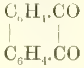
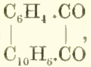
Fittig, on the other hand (B. 6, 168), considered that the quinones were diketones, and assumed that a redistribution of the affinities in the benzene nucleus occurred during the introduction of the oxygen atoms. (Compare the two formulæ for quinone given in the preceding article.)

It is difficult to decide with certainty between these two views, but the great bulk of the evidence is in favour of that of Fittig, which will therefore be adopted in the present article. The formation of quinones by the condensation of fatty α-diketones, and their condensations with two molecules of hydroxylamine hydrochloride to form dihydroximes, can hardly be accounted for on Graebe's view.

Formation.—Many quinones are formed by the oxidation of the corresponding hydrocarbons with chromium trioxide or with potassium bichromate and sulphuric acid:

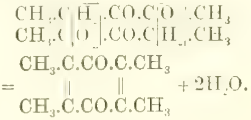


Anthracene Anthraquinone

In like manner naphthalene is oxidised to α-naphthaquinone $C_{10}H_6O_2(1, 4)$. Anthraquinone and α-naphthaquinone are paraquinones; but orthoquinones, such as phenanthraquinone  $\begin{array}{l}C_6H_4.CO\\ |\qquad\ \ |\\ C_6H_4.CO\end{array}$ and chrysoquinone  $\begin{array}{l}C_6H_4.CO\\ |\qquad\ \ |\\ C_{10}H_6.CO\end{array}$, may also be obtained by the oxidation of their hydrocarbons. The reaction takes place with great ease if an agent be employed which chlorinates as well as oxidises, but chloroquinones are formed in this case. Thus benzene, when treated with potassium chlorate and dilute sulphuric acid, yields dichlorquinone $C_6H_2Cl_2O_2$ (Carius, A. 143, 315).

The oxidation to quinones takes place much more readily in the case of hydroxy- and amido-compounds. Phenol, when treated with chromium trioxide in acetic acid solution, yields ordinary quinone: thymol yields thymoquinone $C_6H_2(C_3H_7)(CH_3)O_2$. Aniline gives quinone; α-naphthylamine may be oxidised to α-naphthaquinone. Compounds containing hydroxy- or amido-groups in the para-position to one another very readily yield quinones. Thus *p*-dihydroxybenzene (quinol), *p*-amidophenol, and *p*-phenylenediamine give quinone on oxidation. The relative position of the hydroxy- or amido-groups may determine whether an ortho- or a para-quinone is to be formed. Thus amido-α-naphthol $C_{10}H_6(NH_2)(OH)$ (1, 4) gives α-naphthaquinone $C_{10}H_6O_2$ (1, 4); amido-β-naphthol $C_{10}H_6(NH_2)(OH)$ (1, 2) yields the isomeric β-naphthaquinone $C_{10}H_6O_2$ (1, 2) (Liebermann, B. 14, 1310 and 1795). Metaquinones have not been obtained.

When α-diketones of the general formula $X'.CH_2.CO.CO.Y'$ are warmed with a solution of a caustic alkali, two molecules of the diketone part with two molecules of water and unite to form a para-quinone. Thus acetyl-propionyl yields duroquinone:



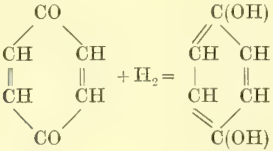
$$\begin{array}{l}CH_3.C\boxed{H_2.CO.C}\boxed{O}.CH_3\\ CH_3.C\boxed{O}.CO.C\boxed{H_2}.CH_3\end{array}$$

$$= \begin{array}{l}CH_3.C.CO.C.CH_3\\ \quad\ \ \|\qquad\ \|\\ CH_3.C.CO.C.CH_3\end{array} + 2H_2O.$$

In like manner, diacetyl $CH_3.CO.CO.CH_3$ forms *p*-xyloquinone $\begin{array}{l}CH_3.C—CO.CH\\ \qquad\ \|\qquad\quad \|\\ \qquad CH.CO.C.CH_3\end{array}$ (von Pechmann, B. 21, 1417).

Properties and reactions.—The quinones are coloured compounds, the colour ranging from yellow to orange and red. They are solid, and may be sublimed or volatilised with steam.

Reducing agents convert the quinones into hydroquinones (quinols), which are dihydric phenols in which the two hydroxyl groups occupy the same positions as the two oxygen atoms of the quinone:



Quinone Quinol.

As intermediate products quinhydrones are formed, the composition of which has not been established with certainty. The same compounds may be obtained by the partial oxidation of hydroquinones with ferric chloride. Owing to this tendency to take up hydrogen, the quinones act as oxidising agents; thus they liberate chlorine and bromine from hydrochloric and hydrobromic acids, but the halogen forthwith replaces hydrogen in the nucleus of the hydroquinone formed:

$$C_6H_4O_2 + 2HCl = C_6H_4(OH)_2 + Cl_2;$$
$$C_6H_4(OH)_2 + Cl_2 = C_6H_3Cl(OH)_2 + HCl.$$

In the case of the perchlorinated quinone this second reaction cannot occur, and the halogen is liberated as such:

$$\underset{\text{Tetrachlorquinone}}{C_6Cl_4O_2} + 2HCl = \underset{\text{Tetrachlorquinol}}{C_6Cl_4(OH)_2} + Cl_2.$$

Phenylhydrazine and free hydroxylamine reduce many of the quinones; but hydroxylamine hydrochloride converts them into dihydroximes: thus ordinary quinone yields $C_6H_4(N.OH)_2$, which when oxidised with an alkaline solution of potassium ferricyanide is converted into *p*-dinitrosobenzene $C_6H_4(NO)_2$ and with fuming nitric acid into *p*-dinitrobenzene $C_6H_4(NO_2)_2$. The dihydroximes of ortho-quinones yield anhydrides: thus when β-naphthaquinone-dihydroxime is heated with dilute acids it parts with water (Goldschmidt and Schmid, B. 17, 2067):—

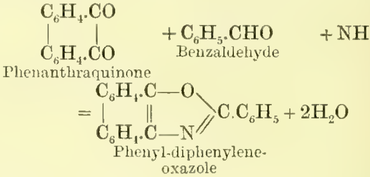
$$C_{10}H_6{<}\begin{matrix}N.OH\\N.OH\end{matrix}\ (1,2) = C_{10}H_6{<}\begin{matrix}N\\N\end{matrix}{>}O + H_2O.$$

Some quinones are not reduced by phenylhydrazine, but react with it, eliminating water: α-naphthaquinone yields with phenylhydrazine benzene-azo-α-naphthol $C_{10}H_6(OH)(N{:}N.C_6H_5)$ (1,4), whilst β-naphthaquinone forms β-naphthaquinone-hydrazone $C_{10}H_6O(N.NH.C_6H_5)$ (1, 2) (Zincke and Bindewald, B. 17, 3026).

With the phenols the quinones unite directly to form coloured compounds belonging to the class of the quinhydrones (*v. supra*).

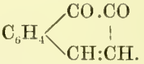
With ammonia and primary amines they react to form sparingly-soluble, more or less highly-coloured compounds which dissolve in concentrated sulphuric acid with a red, violet, or blue colour. Different classes of compounds are formed with different quinones (Zincke).

Orthoquinones differ from paraquinones in reacting with aldehydes and ammonia to form oxazoles:



(Japp and Wilcock, C. J. 37, 669; 39, 225; Japp and Streatfeild, C. J. 41, 157).

Quinones in which there is no hydrogen attached to the nucleus containing the two carbonyl groups are much more stable than those in which hydrogen is present in this condition. Thus, among the paraquinones, anthraquinone $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4$ and duroquinone $C_6(CH_3)_4O_2$ are very stable compounds; and for the same reason, among the orthoquinones, phenanthraquinone $\begin{matrix}C_6H_4.CO\\ | \quad\ \ |\\ C_6H_4.CO\end{matrix}$ is much more stable than β-naphthaquinone



$C_6H_4{<}\begin{matrix}CO.CO\\ |\\ CH{:}CH\end{matrix}$.

F. R. J.

QUINONOXIMES *Nitrosophenols.* Quinonoximes are obtained by treating phenols dissolved in aqueous alkali with sodium nitrite and dilute sulphuric acid (*cf.* Baeyer and Caro, B. 7, 967; Stenhouse and Groves, A. 188, 360; 189, 146; Ilinski, B. 17, 2590), or by treating quinones in aqueous solution with hydroxylamine hydrochloride in the presence of alkali (Goldschmidt, B. 17, 213, 805; Goldschmidt and Schmid, B. 17, 2066; 18, 568, 2224; Auwers, B. 22, 604). Originally regarded as nitrosophenols, *i.e.* $OH.C_6H_4.NO$, inasmuch as they readily undergo oxidation to the corresponding nitrophenols, and reduction to the corresponding amidophenols, they are now usually formulated as quinonoximes, *i.e.* $O{:}C_6H_4{:}N.OH$, on the ground of their ready formation from quinones and ready conversion into quinonedioximes (Nietzki and Kehrmann, B. 20, 616; Nietzki and Guiterman, B. 21, 429); the two formulæ, however, are most probably tautomeric. As a rule, phenols yield quinonoximes containing only one isonitroso- group, but dihydric phenols, with the hydroxyl radicles in the meta- or 1:3- position, except betorcinol, give quinonoximes containing two isonitroso- groups (*cf.* Kostanecki, B. 20, 3133). The quinonoximes of technical importance are dinitrosoresorcinol (*v.* art. Solid green) and the nitrosonaphthols (*v.* art. Naphthalene).

A series of interesting, but technically unimportant, blue, bluish-green, or violet dyes for silk and wool are obtained by condensation of aromatic hydrazo-derivatives with nitrosophenols (Homolka, Germ. Pat. 40369 of June 13, 1886).

QUINOVIN *v.* Glucosides.

R

RACEMIC ACID *v.* Tartaric acid.

RACK-A-ROCK *v.* Explosives.

RADDLE. A kind of red ochre *v.* Reddle.

RAFFINOSE *v.* Melitose.

RAIMONDITE. A hydrated ferric sulphate $2Fe_2O_3.3SO_3.7H_2O$ of a brown-yellow colour, crystallising in thin tabular hexagonal prisms (Breithaupt, J. 1866, 952).

RATANINE *v.* Vegeto-alkaloids.

RAURACIENNE *v.* Azo- colouring matters.

REALGAR. *Ruby sulphur* As_2S_2 *v.* Arsenic.

REAUMUR'S PORCELAIN. Glass in the process of working will often acquire a peculiar opacity. This appears to depend on a physical change, since by a carefully-constructed process a kind of crystallisation may be set up, producing this porcellaneous appearance. Reaumur attempted to introduce a material of this description in the place of pottery (Ure).

RECTIFICATION is the term applied to the second and subsequent distillations of a volatile liquid to free it from the impurities which may have passed over in the first distillation. More particularly applied to the distillation of alcohol (*q. v.*); *v.* also Distillation.

RED, ANILINE, *v.* Triphenylmethane colouring matters.

RED, ANISOLE, *v.* Azo- colouring matters.

RED ANTIMONY. *Antimony oxysulphide* or *kermesite v.* Antimony.

RED, ARCHIL, *v.* Azo- colouring matters.

RED CHALK. An earthy or argillaceous iron ore, used as a drawing or marking material (*v.* Reddle).

RED, CHROME. *Basic lead chromate v.* Chromium.

RED, CLARET, *v.* Azo- colouring matters.

RED, CONGO, *v.* Azo- colouring matters.

RED COPPER ORE. *Native cuprous oxide v.* Copper.

RED, CRESOL, *v.* Azo- colouring matters.

RED, DIAMINE, *v.* Azo- colouring matters.

RED, FAST, *v.* Azo- colouring matters.

RED FIRE *v.* Strontium.

RED HÆMATITE. *Native ferric oxide v.* Iron.

RED, HESSIAN, *v.* Azo- colouring matters.

RED LEAD. *Minium* Pb_3O_4 *v.* Lead.

RED LIQUOR. *Crude aluminium acetate v.* Acetic acid; also Wood, destructive distillation of.

RED MANGANESE. *Native manganous carbonate*, known also as *diallogite v.* Manganese.

RED, NAPHTHIONIC, *v.* Azo- colouring matters.

RED, NEW, *v.* Azo- colouring matters.

RED OCHRE. Oxide of iron mixed with argillaceous matter.

RED OIL *v.* Oleic acid.

RED ORPIMENT. *Realgar v.* Arsenic.

RED, PHENETOL, *v.* Azo- colouring matters.

RED PRECIPITATE. *Mercuric oxide*, HgO *v.* Mercury.

RED SILVER ORE *v.* Proustite and Pyrargyrite; also Silver.

RED, VENETIAN, *v.* Pigments.

REDDLE or **RUDDLE** is a soft, red, iron ore, more or less impure, commonly associated with deposits of hæmatite, as in the Forest of Dean, at Ulverston, and at Whitehaven. It may be regarded as a kind of red ochre, mixed with argillaceous matter, and is used chiefly for marking sheep.

REDONDA PHOSPHATE *v.* under art. Alums; also Manures, artificial.

REDRUTHITE. A variety of cuprous sulphide, known as *chalcosine*, *copper glance*, or *vitreous copper* found in Cornwall, particularly in the neighbourhood of St. Just, in various parts of Scotland, and both crystallised and massive in the porphyritic district in Ulster, and at the Kenmare mines, Kerry.

RED SHORT. Iron and other metals which are brittle at a red heat are said to be red short.

REDUCTION. The abstraction of an electronegative element from, or addition of an electropositive element to, any compound; thus an oxide, deoxidised by the action of hydrogen, charcoal, &c., is said to be reduced. The addition of hydrogen to an organic compound by the action of sodium amalgam, &c., is also called an operation of reduction.

RED WOOD *v.* Brazilwood.

REGINA PURPLE. *Acetate of o-tolyl-p-rosaniline* $C_{28}H_{25}N_3O_4$ *v.* Triphenyl methane colouring matters.

REGULUS. An alchemistic term signifying *the little king*, apparently first applied to antimony. Now used in metallurgy to denote an impure metal obtained from its oxide or sulphide by fusion with a reducing agent.

REHEATING. A metallurgical term mainly applied to the operation of heating puddled bars to a welding heat preparatory to passing them through rolls.

REICHARDTITE. Native hydrated magnesium sulphate, $MgSO_47H_2O$, found at Stassfurt (Krause, Ar. Ph. 376, 41).

RESAZURIN *v.* Phenol colouring matters.

RESINEONE *v.* Resins.

RESIN OIL. *Resin spirit.* Common resin or colophony is a substance which is left in the stills after distillation of spirits of turpentine (*v.* Oils, essential). It is a well-known brittle, but fusible and inflammable, solid which is found in commerce of various colours, from pale yellow to black. It consists of a mixture of acids, the exact composition of which, notwithstanding numerous researches, remains unknown. It is, however, usually regarded as consisting chiefly of abietic anhydride, $C_{44}H_{62}O_4$. These acids form greasy salts with alkalis, and resin is commonly employed as an ingredient in soap, as well as in the manufacture of varnishes.

The lower grades of resin are submitted to distillation with the object of producing an oil, suitable for use as a lubricant, and a spirit which is used in varnish making. The distillation is carried out in cast-iron stills of charging capacity varying between 3 and 10 tons, the usual size being about 5 tons. The head of the still is rounded and provided with flanges by which it can be bolted on to the body, which has a hemispherical bottom. The condensing worm is usually made of copper. A considerable quantity of gas is given off during the distillation, containing carbonic oxide and hydrocarbons. The most volatile portion of the distillate, boiling between 80° and 250°C., constitutes resin spirit or essence of resin, and is followed by the oil, which distils only between 300° and 400°. The residue in the still is pitch or coke, according to the extent to which the heating is carried. From 1 ton of rosin the yield amounts to $\frac{1}{2}$ to 1 cwt. of spirit, and 17 cwts. of oil. Water containing a little acetic acid comes over throughout the distillation, and the crude oils have a milky appearance in consequence.

Resin *spirit* is chiefly used in varnish-making, and as an adulterant of spirit of turpentine. It is refined by agitation with caustic soda and redistillation, or by redistillation only. Crude resin *oil* is a strongly fluorescent viscid oil, about one-fourth of which dissolves in solution of soda, the insoluble part consisting of a hydrocarbon (above 360°). Resin oil has also the property of uniting with slaked lime to form a greasy mass which is used as a lubricant. It is employed chiefly in collieries, and appears to be suitable only for iron bearings. In order to prepare the grease a smooth cream of slaked lime and water is first prepared, and a small portion of the oil is mixed with this in the proportion of about 4 parts of oil to 3 parts slaked lime. The two soon unite, forming a greasy semi-solid mass, with which an additional quantity of oil is afterwards incorporated till the requisite consistence is obtained. The finished grease contains about 1 part of lime to 20–25 parts of oil. The fluorescent bloom of the crude oil can be removed by washing it first with soda lye, and then exposing it to air in shallow iron vessels (Kelbe's patent, Ber. 13, 215a). It is also stated that the bloom can be destroyed by treatment with dinitronaphthalene, with nitrobenzene, or with hydrogen peroxide. Purified resin oil is used to adulterate lubricating oils, and is also mixed sometimes with rape oil and with boiled linseed oil, and forms an ingredient in some printing inks. The resin oils are generally sold under the name 'pine oil,' and are classified, according to quality, as soft, medium, and hard.

The composition of both the essence and the oil has been studied by many chemists. The former consists of a complex mixture of hydrocarbons and other volatile substances, of which, when distilled, resin spirit generally yields more than half its volume below 120°C. The following constituents have been isolated: A pentine, C_5H_8 (b.p. 50°) (Couerbe, J. pr. 18, 165); isobutyl-aldehyde (Tilden, B. 13, 1604); isobutyric, caproic and other fatty acids, methyl alcohol, (very small quantity, 50 grms. from 150 kilos); a hydrocarbon, C_9H_{12} (b.p. about 160°), homologue of benzene; ordinary cymene and a new cymene (metapropyltoluene); metaisobutyltoluene (b.p. 186–188°); parabutyl-toluene (b.p. 176–178°) (Kelbe, B. 13, 888, and 1157; A. 210, 1; B. 14, 1240; B. 15, 308); dipentine, $C_{10}H_{16}$ (Tilden, B. 13, 1604) together with a relatively large proportion of a heptine, C_7H_{12} (103–104°), which has been shown by Morris (C. J. 1882) to be probably methyl-propyl-allene $CH_3.CH{:}C{:}CH.C_3H_7$. This liquid is characterised by giving a succession of colours (yellow, red, green, and deep blue) when agitated with strong sulphuric or hydrochloric acid. In the presence of air and water it forms a glycol, $C_7H_{12}(OH)_2$, which crystallises with one molecule of water in the form of long slender prisms, which are frequently to be seen in old samples of resin spirit.

Resin oil consists of a mixture of abietic acid $C_{44}H_{64}O_5$ (m.p. 165°), and small quantities of phenols with a hydrocarbon or mixture of hydrocarbons $(C_{10}H_{16})_n$ (b.p. above 360°), which constitutes about three-fourths of the whole.

W. A. T.

RESINONE *v.* RESINS.

RESINS. Resins constitute a class of vegetable or (sometimes) animal products which are solid or semi-solid, insoluble in water, but generally soluble in alcohol, ether, and volatile oils. They nearly all begin to soften at temperatures much below their melting-points. They are often left by the spontaneous evaporation of oleoresinous juices which exude either naturally or by incision from the trunks of trees. A number are found as minerals, but these are undoubtedly the product of extinct vegetation. Others are extracted from various parts of plants by such solvents as alcohol and ether. This article excludes those resins which contain benzoic or cinnamic acid (*balsams*), those which appear in commerce admixed with gum (*gum resins*) or volatile oil (*oleoresins*), and those which consist of hydrocarbons allied to *petroleum*. It is perhaps to be regretted that it is necessary to retain such a classification as this, based as it is upon commercial or botanical considerations, or at best upon physical distinctions of solubility. Chemical inquiry has not, however, yet been carried far enough to make a more scientific arrangement possible, and, indeed, so widely do the various resins that have been studied differ from one another chemically that it seems likely that as a class they will ultimately disappear, being taken to fill in gaps here and there in the growing structure of organic chemistry.

We shall here treat of the more important representatives of this group of substances. For those which are less known, see the various Reports on Botanical Economics, Museum Catalogues, also Gm. (17, 382) and Bn. (3, 311). On the formation of resins see Heldt (A. 63, 48), Wiesner (Sitz. W. 52, 2, 118), and Barth (Z. 1867, 508); their composition and behaviour towards reagents, Rose (A. 13, 174), Johnston (A. 44, 328); the compounds formed by the action of melted potassium hydroxide, Hlasiwetz and Barth (A. 134, 265; 138, 61; 139, 77); their neutralisation or saponification coefficients when treated with a standard solution of caustic alkali, Kremel (Fr. 26, 262; Ph. [3] 17, 547); their respective iodine absorption numbers, Williams (C. N. 58, 224); determination of their methoxyl equivalents, Bamberger (M. 11, 84), and on the systematic identification of resins, see Hirschsohn (P. Z. 16, 81; 24, 529; Fr. 17, 256) and Schmidt and Erban (M. 7, 665).

Alouchi, or Aluchi Resin. A resin imported from Madagascar. It is friable, dirty-white externally, blackish and marbled within, and has a bitter, peppery taste. It was examined by Bonastre (J. Ph. 9, 180; 10, 1), who found it soluble in cold alcohol to the extent of 68·12 p.c. A further portion, 20·45 p.c., dissolved in hot alcohol. It contains a small quantity (1·6 p.c.) of essential oil. *V.* also Vauquelin (A. Ch. 72, 299).

Arnica Resin, *Arnicin.* The root of *Arnica montana* (Linn.), a compositous plant inhabiting the northern and central regions of Europe and America (Bentl. a. T. 158), contains a resinous substance to which the name *arnicin* has been given, together with *gum, wax, inulin* 10 p.c., *volatile oil,* and an alkaloid (?) *arnicine* (Bastick, Ph. 10, 386), and other constituents. The resinous compound arnicin was isolated by Walz (N. J. P. 13, 175; 14, 79; 15, 329). It is yellow, amorphous, has an acrid taste, is soluble in alcohol, ether, and alkalis, and is precipitated from the alcoholic solution by water. Analysed, it gave numbers corresponding to the formula $C_{20}H_{30}O_4$. It may possibly prove to be a glucoside. For another constituent to which the name 'arnicin' has been given, *v.* Parvesi (J. 1859, 584); and for other resins Gm. (17, 363 a. 447).

Betula Resin, *Betulin.* The outer bark of the birch tree *Betula alba* (Linn.) yields a resin. Löwitz, in 1788, described it (Crell's Ann. 2, 312), and it has been further examined by Hünefeld (J. pr. 7, 53), Hess (A. 29, 135), Mason (B. J. 12, 248), Stähelin and Hofstetter (A. 51, 79), Housmann (A. 182, 369), and others. Betulin melts at 258°, and has the formula $C_{36}H_{60}O_3$.

Capsicum Resin. The fruits of *Capsicum fastigiatum* (Blume) and *Capsicum annuum* (Linn.), constituting respectively the small and large red or cayenne pepper pods of commerce, yield a *resin* to which the acrid property of the pods was once attributed (Buchholz and Braconnot, Gm. 17, 450). The other important constituents are a *volatile oil,* a volatile alkaloid, *capsicine,* which resembles coniine (Felletár, J. Ph. 1870, 347; Thresh, Ph. [3] 6, 941), and an intensely active acrid, crystalline compound discovered by Thresh, *capsaicin,* to which the pungency of cayenne pepper is now ascribed (Ph. [3] 7, 21, 259 a. 473; 8, 187). Capsaicin has the formula $C_9H_{14}O_2$. It does not possess basic properties. It melts at 59°, sublimes at 115°, and has a sp.gr. of 1·060. Most solvents, including sulphuric and glacial acetic acids, dissolve capsaicin; but it is insoluble in water, and is thrown out of its solution in alkalis by a stream of carbonic acid gas. *V.* also Meyer (Ph. Z. 1889, 130).

Castoreum Resin. The dried preputial follicles of the beaver, *Castor fiber* (Linn.), are used in medicine as a nervous stimulant or antispasmodic (Pereira, Mat. Med. 1853, 2, 2266). Castor contains a *resin,* 1–2 p.c. of *volatile oil,* and a neutral crystalline substance, *castorin.* If castor be treated with hot alcohol, either with or without previous admixture with lime, a solution results which, on cooling, deposits castorin in crystals, and from the mother-liquor of which the resin may be obtained by the addition of water. Castorin was discovered by Bizio (Ar. Ph. 11, 112), and further investigated by Valenciennes (Ph. 1861, 329). It is neither acid nor basic, and assumes the form of easily-fusible needles which possess only in a faint degree the odour and taste of castor. The activity of castor resides in the resin, which, having been precipitated by water from the alcoholic solution, from which the castorin has been separated, may be purified by re-solution in alcohol and re-precipitation by water. The yield varies very much, some specimens of castor giving as much as 58 p.c., and others not more than 14 p.c. Castor resin is nearly black. It is brittle, and is insoluble in ether. It possesses the bitterness and acridity of castor in a very high degree. The volatile oil obtained, to the extent of 1 or 2 p.c., by distilling castor with water is pale-yellow and viscid, is nearly insoluble in water, but soluble in alcohol, and possesses the odour of the drug (Gm. 15, 364). With regard to the supposed presence of an *alkaloid* in castor, *v.* Reuter (Ph. Centh. 1889, 305). Many other constituents, in small quantity, have been announced from time to time as occurring in castor, such as bile, salicin, benzoic acid, and phenol.

Colophony (*Common Resin*; *Rosin*; *Resina,* Br. Ph.; *Colophane,* Fr.; *Kolophonium,* Ger.). Colophony is the residue which remains after the volatile oil has been removed by distillation from the oleoresins, the crude turpentines which exude from various species of coniferæ. It varies somewhat, according as it is derived from the one or the other species, and with the method employed for its production. The browner resins are mostly of American origin, from *Pinus australis* (Michaux); while those of a lighter colour come by way of Bordeaux, being the yield of *Pinus Pinaster* (Solander), an inhabitant of the districts of the Landes and the Gironde. It varies in colour from pale amber to dark red-brown. The 'white resin' of commerce owes its light-yellow colour to a slight opacity, due to the presence of small quantities of water.

Colophony is a very brittle solid with a glassy fracture. It has a faint odour of turpentine, and scarcely any taste. It is heavier than water, in which it is insoluble. Its sp.gr. is generally 1·07. Ether, chloroform, acetone, benzene, volatile, and fixed oils dissolve it readily, and at 60° it is soluble in its own weight of alcohol or glacial acetic acid. It is soluble in alkalis. It softens at 80°, and melts variously from 100° in some specimens to 135° in others. Heated to higher temperatures by itself it yields gaseous products and a distillate of *resin oil,* but in a current of steam above 200° colophony may be distilled without any appreciable change.

Common resin consists, as Maly and, subsequently, Flückiger have shown, essentially of *abietic anhydride* (A. 129, 94). When the coarsely-powdered resin is agitated with warm dilute alcohol, the anhydride is hydrated, and 80 to 90 p.c. of it is converted into crystalline *abietic acid* $C_{44}H_{64}O_5$. The resin itself has the formula $C_{44}H_{62}O_4$. Emmerling (B. 12, 1441) obtained the acid, which he regenerated from its ammonium salt, as a snow-white powder; but, more recently, Kelbe (B. 13, 888) has succeeded in getting it to assume the form of triclinic prisms by crystallisation from a solution in glacial acetic acid. Abietic acid melts at 139° (E.), 165° (M.; K.). It forms metallic and alkyl derivatives (Bn. 2, 1259). The corresponding acid constituent of Russian pine resin, the product of *Pinus sylvestris* (Linn.), appears to be similar but not identical with abietic acid (Shkateloff, J. R. 20, 477).

When colophony dissolves in alkali, an alkaline abietate, or *resin soap*, is formed. This is largely employed as an admixture in the manufacture of the commoner soaps. Heated to redness colophony evolves a mixture of gases, which burns with a bright flame, and it has been proposed as a source of illuminating gas. It enters largely into the constitution of the less-esteemed varnishes, is used for the caulking of ships, for cements, as a reducing agent in the soldering of metals, and in pharmacy it enters into many ointments and plasters.

The *resin* or *rosin oil* obtained by the dry distillation of resin is widely made use of, and its chemical constituents are being more and more studied. It consists essentially of a mixture of hydrocarbons and fatty acids. Generally it is separated into two portions, the lighter spirit that first comes over being collected apart from the heavier oil, which distils last. The lighter spirit is used as a substitute for oil of turpentine, while the heavier is employed as a lubricant and in soap-making. The lighter *resin spirit*, boiling below 360°, contains, according to Renard (A. Ch. [6] 1, 223), the following compounds: pentane, boiling from 35° to 38°, amylene (35–40°), the hydrocarbons C_6H_{14} (64–66°) and C_6H_{12} (67–70°), hexahydrotoluene (95–98°), tetrahydrotoluene (103–105°), toluene (111°), hexahydroxylene (120–123°), tetrahydroxylene (128–130°), xylene (136°), hexahydrocumene (147–150°), the hydrocarbon C_9H_{16} (155° ?), cumene (151°), terpenes (154–157° and 171–173°), hexahydrocymene (171–173°), cymene (175–178°), (m)ethylpropylbenzene (193–195°), the hydrocarbon $C_{16}H_{28}$ (about 260°), isobutyric aldehyde (60–62°), valerianic aldehyde (96–98°), also isobutyric acid and valerianic acid. Colophene (318–328°), the compound formed by polymerising turpentine oil by means of sulphuric acid, is also a constituent of resin spirit (Deville, A. 37, 193). The heavier *resin oil*, boiling above 360°, consists of hydrocarbons together with a mixture of acids and phenols and much undecomposed colophony. For other constituents of resin oil see Tilden (B. 13, 1604), Kelbe (A. 210, 12), Kelbe and Lwoff (B. 16, 351), and Lwoff (B. 20, 1020), Brownsword and Cohen (S. C. I. 1890, 16). The gases evolved during the distillation have been examined by Schiel (A. 115, 96). When the resin oil boiling from 103–104° is allowed to stand in contact with air and water, a crystalline solid, colophonium hydrate, is formed, having the composition $C_{10}H_{22}O_3,H_2O$. It melts at 106° and sublimes with some decomposition (Tichborne, Ph. [3] 1, 302; Anderson, J. 1869, 787; Tilden, B. 13, 1604). According to Bischoff and Nastvogel (B. 23, 1919), the breaking up of colophony by destructive distillation is much simpler if the operation be performed under reduced pressure. In this case the products are chiefly two: one a hydrocarbon, $C_{20}H_{32}$, boiling at 218–220° (30 mm.), which is probably colophene; the other, a liquid, which slowly solidifies to a mass of microscopic crystals having the composition $C_{40}H_{58}O_3$, is the anhydride of an isomeride of sylvic acid. The anhydride dissolves in potash solution, and from the salt thus formed isosylvic acid, $C_{20}H_{30}O_2$, melting at 60·5–62·5°, is obtained by treatment with acetic acid. For methods of detecting the presence of resin oil in fixed or volatile oils, see Storch (S. C. I. 1888, 136), Holde (S. C. I. 1888, 526; 1890, 419, Morawski (S. C. I. 1889, 572), Baudin (J. Ph. [5] 23, 279), Chenevier (S. C. I. 1890, 825), and Gilbert (Chem. Z. 13, 1428).

When resin is distilled with lime, another series of compounds is produced (Fremy, A. Ch. 59, 13; Bruylants, B. 8, 1463; 11, 448). For production of benzene by distillation of resin with superheated steam, *v.* Watson Smith (C. J. 30, 29); for distillation of resin with sulphur, *v.* Currie (J. 1874, 921); and for products of the oxidation of resin with nitric acid, *v.* Schreder (A. 172, 93) and Vogel (J. 1869, 785).

Resin is largely used as an adulterant. For methods for its detection and estimation, see—Resin in Soap: Senier (Am. J. Pharm. [4] 4, 353), Gladding (Am. 3, 416), Heiner (J. Ph. [5] 11, 434), Wright and Thompson (C. J. Proc. 2, 175), Grittner and Szilasi (Chem. Z. 10, 325), Morawski (S. C. I. 1888, 891; 1889, 592; Chem. Z. 12, 1321), Holde (S. C. I. 1889, 592), Twitchell (S. C. I. 1891, 804). Resin in Fats: Gladding (Am. 3, 416), Focke (C. C. 1886, 44). Resin in Wax: Schmidt (Seifensieder, Z. 17, 197), Morawski. Resin in Mineral Oil: Valenta (D. P. J. 252, 296), Morawski.

Common Frankincense (*Gum Thus*; *French Pine Resin*; *Galipot*, Fr.). The crude turpentine which concretes on the trunks of the French pine trees was scraped off and employed in pharmacy. The greater part of the Gum Thus of commerce is now, however, derived from American sources. This French resin, which alone has been studied, does not consist of the anhydride of abietic acid, but, as it now appears, of a group of nearly-related pimaric acids. These have been investigated by Laurent (A. Ch. [2] 72, 384; [3] 32, 459), Maly (A. 129, 94; 132, 253; Z. [2] 5, 304), Duvernoy (A. 148, 143), Sievert (J. 1859, 510), Strecker (A. 150, 131), Bruylants, B. 11, 448), Caillot (Bl. 21, 387), Liebermann (B. 17, 1884), Haller (B. 18, 2165), and by Vesterberg (B. 18, 3331; 19, 2167). The last-named observer finds that what has hitherto been termed 'pimaric acid' is in fact a mixture of at least three acids. The one, α- or *dextro-pimaric acid* $C_{20}H_{30}O_2$, he obtains in crystals melting at 210 to 211°. It is a monobasic acid, and forms metallic and ethereal salts, also acid radicle derivatives. A characteristic property is the formation of a beautiful crystalline ammonium salt which falls when a few drops of ammonium hydroxide are added to the solution of the acid in ether. *β-pimaric acid* resembles Caillot's pimaric acid. It is crystalline, and melts at about 150°. *γ-pimaric acid* has been but little studied.

Copal Resin. Copal is the concrete exudated juice of various trees. It is obtained either directly from the trees or as a fossil resin buried in the earth in their neighbourhood. Fossil copal is a highly-prized variety. It comes from the East Indies, South America, and both the east and west coasts of Africa. The South American resin is known in English markets as 'Animi Resin' or 'Gum Animi.' The precise botanical origin is uncertain. Some copals are soft. These are obtained from Sumatra, Java, Molucca, the Philippines, and Australia, and they are soluble in ether. The hard copals, which do not dissolve in ether until they have undergone a chemical change, come by way of Calcutta from Zanzibar and the African coast, and by way of Bombay from Madagascar, Mauritius, and Bourbon. Hard copal varies in properties somewhat with the origin of the different resins which are known by that name; but generally it is of a light-yellow or brown colour, without taste or smell, and has always been prized for varnishes. It occurs in roundish or flattish pieces, more or less transparent, and breaks with a conchoidal fracture. The sp.gr. varies from 1·045 to 1·139, but it is generally between 1·059 and 1·072. In the crude state hard copal is insoluble in alcohol, and only partially soluble in ether or oil of turpentine. When, however, the crude resin is heated, gases are evolved, and a residue remains which dissolves readily in ether and oil of turpentine. In making varnishes, copal is melted and heated slightly, and hot turpentine slowly run into the melted resin.

Hard copal, according to Unverdorben (B. J. 11, 265) and Filhol (A. 44, 323), is a mixture of five resins. Its behaviour when heated in closed tubes was studied by Violette (C. R. 63, 461). Submitted to destructive distillation, it yields a terpene boiling at 160–165° and a heavier oxygenated oil (Schibler, A. 113, 339). Friedburg (A. C. J. 12, 285 a. 392), who has recently investigated copal, finds that when distilled, a terpene, probably limonene, comes over between 100° and 185°, and that above that temperature decomposition takes place till 215° is reached, when the thermometer falls suddenly to 170° and a dark residue remains. The same observer notes that with benzaldehyde copal forms a solution which gelatinises, and from which on distillation an oil is obtained which condenses in white crystals; also that the resin reacts energetically with alcoholic ammonia, giving rise to an ammonium salt which is entirely volatile.

Dammara Resin (*East Indian Dammara Resin*; *Dammar Puti*). This variety of dammar resin is derived probably from *Pinus dammara* (Lambert), a coniferous tree indigenous to the East Indies and the Moluccas. The resin exudes and dries on the trees in lumps of various shapes and sizes, and is collected. It is partially soluble in alcohol, more so in ether, and almost completely in fixed and volatile oils. It is entirely soluble in sulphuric acid. The resin was examined by Dulk (J. pr. 45, 16) and Schrötter (P. 59, 72).

When crude dammar is treated with weak alcohol, a portion, about one-third, dissolves; this is the *α-resin* or hydrated *dammarylic acid* of Dulk. Its formula is $C_{45}H_{74}O_4$. It is a white powder which melts at 50°. From the residue, absolute alcohol extracts the *β-resin* or anhydrous *dammarylic acid* $C_{45}H_{72}O_3$, which is also a white powder. Its melting-point is 60°. By treatment of the residue with ether, according to Dulk, a hydrocarbon *dammaryl* $C_{45}H_{72}$ is dissolved. Dammaryl is a tasteless, inodorous powder which softens at 145° and melts at 190°. When it is exposed to the air it undergoes oxidation until a body is formed having the composition of the original resin. A residue remains after the treatment with ether, which is the *γ-resin* or *semihydrate of dammaryl*, a shining brittle resin which melts at 215°. The presence of a free hydrocarbon in dammar is, however, denied by Graf (Ar. Ph. [3] 27, 97), who finds the resin to consist of about 60 p.c. soluble in alcohol, melting at 61°, 40 p.c. insoluble in alcohol, melting at 144° to 145°, and about 1 p.c. of a dibasic acid. *V.* also Franchimont (Bn. 3, 314).

Australian Dammara Resin, *Australian Copal*, *Kauri*, *Kawrie*, or *Cowdie Gum*. This is the product of *Dammara australis* (Lambert), a coniferous tree which inhabits New Zealand, where the dammar is found as a fossil resin (*v.* Robinson, Ph. [3] 19, 306). The resin examined by Thomson (A. Ch. [3] 9, 499) was found to consist of an acid resin, *dammaric acid* $C_{40}H_{62}O_7$, and a neutral resin, *dammaran* $C_{40}H_{62}O_6$. The acid is extracted from the crude dammar by alcohol. Distilled alone, Australian dammar yields a volatile oil, *dammarol*, and, distilled with lime, another oil, *dammarone*. Rennie, distilling kaurie resin with water, obtained a *terpene* boiling at 157–158° (C. J. 39, 240), and the action of chlorine and bromine and of nitric acid on the resin has been studied by Muir (C. J. 27, 733).

Dragon's Blood Resin. *Resina Draconis.* (*Sangdragon*, Fr.; *Drachenblut*, Ger.) The name 'dragon's blood' has been employed from ancient times to designate various red resinous exudations, but it is now chiefly applied to the crimson-red resin which exudes and dries on the fruits of the rotany or rattan palm, *Calamus Draco* (Willdenow), of the East Indies. The drug appears in commerce for the most part in two forms—the one consisting of sticks of resin wrapped in palm leaves, the *reed dragon's blood*; the other, the *lump dragon's blood*, being blocks or irregular-shaped masses (Fl. a. H. 673). Dragon's blood has a sweetish, somewhat acrid taste, and melts at about 120°, when it is said to evolve benzoic acid. It dissolves in alcohol, benzene, chloroform, carbon bisulphide, glacial acetic acid, and caustic soda. In petroleum ether it is insoluble, and it dissolves but sparingly in oil of turpentine or ether. It is employed as a colouring agent in pharmacy, and for varnishes.

Among other resins to which the name dragon's blood has been given are: *Socatrine Dragon's Blood*, obtained from trees of the genus *Dracæna* in the island of Socatra (Balfour, Ph. [3] 14, 372); *Canary Islands Dragon's Blood*, derived from *Dracæna Draco* (Linn.); and *West Indian Dragon's Blood*, which is produced by *Pterocarpus Draco* (Linn.); and *Croton Draco* (Schlecht) (*v.* Fl. a. H.). According to Dobbie and Henderson (Ph. [3] 14, 361), who examined a large number of specimens, the dragon's blood of commerce consists of four distinct products. The *Calamus*, or East Indian resin, agreed with the characters given above, except that it was freely soluble in ether.

The resins of dragon's blood were analysed by Johnson (Tr. 1839, 134; 1840, 384), and the numbers obtained agree with the recent results obtained by Dobbie and Henderson (*v.* Herberger, Buch. Repert. 37, 17; 40, 138). The resin does not contain benzoic acid, as earlier investigators had supposed, but some varieties appear to contain cinnamic acid (Dobbie a. Henderson, Hirschsohn, P. Z. 16, 1, 33, 65 a. 97).

Blyth and Hofmann (C. J. 2, 334) found toluene and styrene among the products of the destructive distillation of dragon's blood (*v.* Glénard a. Boudault, C. R. 17, 503; 19, 505). When fused with potash the resin yields benzoic and (*p*)-hydroxybenzoic acids and phloroglucinol (Hlasiwetz a. Barth, A. 134, 283); distilled with zinc-dust, styrene, toluene, and other products (Bötsch, M. 1, 609), and by the action of nitric acid, oxalic, and nitrobenzoic acids (Blumenau, A. 67, 127).

Ergot of Rye Resin. Ergot contains a resin, to which at one time its activity was thought to be due (*v.* ERGOT).

Eucalyptus Resin. Obtained from the leaves of *Eucalyptus globulus* (Labill.). It is coloured carmine-red by sulphuric acid (Hartzer, B. 9, 314).

Fossil Resins. *Amber, Succin, Bernstein.* A hard, generally yellow or orange resin thrown up by the sea, along the Baltic coast, especially in Prussia, and in smaller quantities throughout the world (*v.* Rose, A. 28, 339). Amber is tasteless and brittle, and admits of a fine polish. It is much used as an ornament. It becomes negatively electric by friction. The sp.gr. of amber varies from 1·05 to 1·10, and it ranks 2 to 2·5 in the scale of hardness. It is insoluble in water, alcohol, essential oils, and acids, with the exception of sulphuric. When, however, it is first subjected to heat, it undergoes a change like copal, and becomes soluble in alcohol and turpentine oil. There can be no doubt that amber is the fossil resin of extinct coniferæ (Göppert, A. 21, 71). The character of the insects which it includes, and which often render it very beautiful, are an evidence in support of this view.

Berzelius (B. J. 8, 231) found amber to consist of *succinic acid* (3 to 8 p.c.), a little *volatile oil, two resins*, one soluble in ether, the other insoluble but soluble in alcohol, and an *insoluble residue* (*v.* Forchhammer, A. 41, 47; Schrötter, B. J. 24, 593). It contains 0·24 to 0·48 p.c. of sulphur (Baudrimont, J. 1864, 538). When heat is applied to it there is evolved, in the first place, succinic acid, water, oil, and combustible gases; the residue is then soluble in alcohol and oil of turpentine. A further application of heat brings over a colourless oil, *oil of amber*, which, when the distillation is well managed, amounts to 28 p.c. of the original resin. Finally, when the temperature rises at the close of the operation, a yellow *wax* condenses. Oil of amber is a mixture of several hydrocarbons. The lighter portion is coloured blue by hydrochloric acid, and decomposed by sulphuric acid; while the heavier portion is unacted on by these reagents. Pelletier and Walter (A. Ch. [3] 9, 89) find these oils to be isomerides of oil of turpentine. The wax-like solid consists of oil, chrysene, a white crystalline body, *succisterene*, and brown bitumen. These were isolated by Pelletier and Walter by the use of alcohol and ether (*v.* Bley a. Diesel, J. 1847–48, 736). When amber is distilled with potash, a watery liquid passes over, and, finally, a solid condenses which has all the properties of *camphor* (Berthelot a. Buignet, C. R. 50, 606; Reich, J. Ph. 13, 33; Döpping, J. Ph. 6, 168).

A commercial *substitute for musk* is prepared from amber, or oil of amber, by the action of fuming nitric acid. It is a resinous-looking solid which, washed to remove excess of acid, is soluble in alcohol and essential oils. It has a burning, aromatic taste, and musky odour. This substance was discovered by Marggraf (A. Ch. 73, 182), and was investigated by Elsner (J. pr. 26, 97), Foltz (R. P. 4, 226), and Marsson (Ar. Ph. [2] 62, 8). As to its use in medicine and its preparation for this purpose, see Williams (Am. J. Pharm. 8, 14). It has not been ascertained whether this artificial musk obtained from amber is in any way related to the *artificial musk* of Bauer (B. 24, 2832), which is now an article of commerce. The latter is derived from butyltoluene, a constituent of resin spirit, by the action of nitric and sulphuric acids. It is a trinitrobutyltoluene $C_6H(CH_3)(C_4H_9)(NO_3)_3$, and crystallises in yellowish-white needles, which melt at 96–97°.

Amber was formerly much esteemed in medicine; but it is now used chiefly as an ornament, sometimes for photographic and fine varnishes, and in pharmacy as a source of oil of amber and succinic acid.

Ambrite. The lignite formation in Auckland, New Zealand, furnishes this resin in large lumps. It is brittle, semi-transparent, and of a yellowish-grey colour. Its sp.gr. is 1·034, and its hardness 2. It is insoluble in most solvents, but dissolves partly in carbon bisulphide. It is said to have the composition $C_{16}H_{26}O_2$ (Hauer and Maly, J. 1866, 1034).

Anthracoxene. This resin is found between the coal strata near Schlau in Bohemia. When seen in masses it is brownish black in colour, but in thin layers is hyacinth red. It is brittle and swells when heated. According to Laurentz anthracoxene is a mixture of several resins (Sitz. B. 21, 271; J. pr. 69, 428).

Asphalt. This substance, found by the shores of the Dead Sea, is probably the result of the decomposition of vegetable matter, and is closely allied to petroleum. *V.* PITCH.

Berengelite, Berengela resin. A bituminous resinous mineral found in Peru. It is used for caulking ships. It has a dark-brown colour and is soluble in alcohol and ether, and melts below 100° (Johnston, P. M. [3] 14, 87).

Boloretin. Derived from the fossil fir wood found in the Danish peat bogs. It is soluble in ether but not in cold alcohol, and melts at 75° to 79° (Forchhammer, A. 41, 44; *v.* Krämer, Ar. Ph. [2] 27, 73).

Brusterort Resin, Unripe amber. This fossil resin resembles krantzite and differs from amber in not containing succinic acid (Spirgatis, J. 1871, 1188; 1872, 1146).

Bucaramanga Resin. Boussingault examined this resin (A. Ch. [3] 6, 507). It comes from Bucaramanga in New Granada. In appearance it resembles amber, but it does not contain succinic acid.

Copalin, Highgate resin. The blue clay of Highgate Hill contains roundish lumps of this fossil resin. It was studied by Johnston (P. M. [3] 14, 87) and Bastick (Ph. 8, 339). It resembles copal. Similar resins have been found in India and in the lead mines of Northumberland (Dana, 2, 267).

Euosmite. An aromatic resin found in the lignite of Thumsenreuth in Bavaria. It consists of brownish yellow pulverulent masses or lumps (Gümbel, Gm. 17, 436).

Guayaquillite. From Guayaquil in South America (Johnston, P. M. [3] 13, 329).

Hartin. A white, inodorous, and tasteless resin found in the lignite of Oberhart, Austria. It is said to have the composition $C_{10}H_{17}O$ (Schrötter, P. 54, 45).

Hartite. Another resin found in the same place as hartin. According to Schrötter (P. 54, 45), it consists of a hydrocarbon of the formula C_3H_5. Hartite has also been investigated by Haidinger (P. 54, 261), and by Rumpf (J. pr. 107, 189).

Ixolite. Occurs together with hartite (Hardinger, P. 56, 345).

Jaulingite. From Jauling in Austria (Ragsby, Sitz. B. 16, 366).

Krantzite. This is a variety of retinite (Bergemann, J. pr. 76, 65).

Middletonite. The coal seams near Leeds and at Newcastle contain this resin. It was analysed by Johnston (P. M. [3] 12, 261). Two similar fossil resins found in the coal measures were examined by Macadam (C. N. 59, 1).

Pianzite. An earthy resin examined by Haidinger (P. 42, 275). Hardness 1·5, sp.gr. 1·22, and m.p. 315°.

Pyroretin. A brown resin from the lignite of Salesl, near Aussig in Bohemia (Stanek, Sitz. B. 12, 551).

Retin Asphalt. This is a yellow-brown earthy-looking resin, the sp.gr. of which varies from 1·07 to 1·35. That from the lignite of Bovey in Devonshire was examined by Hatchett (Tr. 1804, 404) and later by Johnston (Tr. 1840, 347). Johnston found it to consist of 13·23 p.c. mineral matter, 27·45 p.c. resin insoluble in alcohol and 59·23 p.c. resin soluble in alcohol. The resin soluble in alcohol gave the formula $C_{40}H_{54}O_6$, and was called by Johnston *retinic acid.* Other varieties of retin asphalt occur in the neighbourhood of Halle in Germany (Bucholz, Schw. J. 1, 290) and near Cape Sable in the United States.

Retinite, Walchovite. This resin, of which there are several varieties, occurs in the coal mines of Walchow in Moravia (Schrötter, P. 59, 61; Cerutti, Ar. Ph. [2] 22, 286).

Schleretinite. Obtained from the coal mines of Wigan (Mallet, P. M. [4] 4, 261).

Tasmanite. The aluminous rocks along the Mersey river in Tasmania yield small scales or plates of this resin. It contains sulphur, and, according to Church (P. M. [4] 28, 465), has the formula $C_{40}H_{62}O_2S$.

Val d'Arno Superiore Resin. This fossil resin, called by the peasantry 'terra che brucia,' closely resembles the Weissenfels resins. Alcohol separates it into *α-resin* $C_{40}H_{64}O_8$ melting at 75–90°, and *β-resin* $C_{40}H_{58}O_5$, which melts above 120° (Guareschi, Cimento, 5, 175).

Xyloretin. A crystalline resin having the formula $C_{10}H_{16}O$ found in the fossil pine trunks of the Danish peat-bogs. It is insoluble in water, soluble in alcohol, and melts at 165°. Heated with potassium it gives a metallic derivative, with liberation of hydrogen (Forchhammer, A. 41, 42; *v.* Schrötter, P. 59, 54).

Resins of Weissenfels Lignite. A series of resinous substances have been isolated from the products of distillation of this lignite. They have been investigated by Brückner (J. pr. 57, 1) and Wackenroder (Ar. Ph. [2] 60, 23).

Guaiacum Resin. *Resina guaiaci.* (*Résine de Gaïac*, Fr.; *Guaiakharz*, Ger.) Two West Indian species of guaiacum tree, *G. officinale* (Linn.) and *G. sanctum* (Linn.), yield the resin, (Fl. a. H. 100; Bentl. a. T. 41). It is obtained partly as a natural exudation, partly by means of incisions, and in some places the trees are cut down and the trunks set on fire at each end, when the warm resin exudes freely from incisions made in the middle. In commerce guaiacum resin appears in 'tears' or in masses. It is brittle, and, though at first of a reddish colour, it becomes greenish by superficial oxidation (*v.* Schiff, A. 111, 372). It has a faint balsamic odour, though it contains no benzoic or cinnamic acid. The sp.gr. is 1·20 and it melts at 85°, when the balsamic odour is more marked. The resin is soluble in alcohol, ether, acetone, chloroform, and in caustic alkalis; but in benzene and carbon bisulphide it only dissolves partially. Solution of guaiacum resin in alcohol is a very sensitive reagent for oxidising agents. Ferric chloride, for instance, strikes with such a solution a dark-blue colour. Reducing agents discharge the colour, which reappears on oxidation (*v.* Schönbein, Fr. 8, 67; J. pr. 102, 164; Schaer, Fr. 9, 430; Schönn, Fr. 9, 210). According to Kowalewsky (C. C. 1889, 210), the action of ozone on the resin gives rise, not simply to a blue-coloured product, but to a series of colours of which blue is about the middle member. This observer notices that the presence of moisture is necessary, that ozone gives no colour with dry guaiacum (*v.* Hager, Fr. 26, 261). The solution is not coloured blue by peroxide of hydrogen, a reaction which serves to distinguish that compound from ozone. In presence of such a substance as blood, however, the blue colour appears. If a spot of blood be moistened with freshly prepared alcoholic solution of the inner unoxidised portions of guaiacum resin, and then with an ethereal solution of peroxide of hydrogen, a blue colour is produced which can often be made more evident by transference to white blotting paper. This property of guaiacum is often resorted to as a *means of identifying blood stains.* For method of testing guaiacum resin, *v.* Hager (Fr. 26, 261).

Crude guaiacum resin heated with an alcoholic solution of caustic potash yields a salt of *guaiaretic acid* $C_{20}H_{26}O_4$, which falls to the bottom of the vessel in a crystalline form (Unverdorben, P. 16, 369). The free acid constitutes 10 p.c. of guaiacum resin. It is insoluble in water, but is soluble in alcohol, ether, and most solvents. It melts at 80°, may be distilled unchanged, and is not coloured blue by oxidising agents. A bromine derivative and numerous metallic salts have been prepared. (Hlasiwetz, A. 112, 182; 119, 266). If the alcoholic mother-liquor from the potassium guaiaretate be treated with hydrochloric acid a heavy amorphous precipitate falls, which after washing, yields to ether the α-resin or *guaiaconic acid* $C_{38}H_{40}O_{10}$. This constitutes 70 p.c. of the crude resin. It was isolated by Hadelich (J. pr. 87, 321), who prepared a lead salt. It melts at 100° and decomposes alkaline carbonates. In water, benzene, and carbon bisulphide it is insoluble, but it dissolves in alcohol, ether, chloroform, and acetic acid. It is turned blue immediately by oxidising agents. After treatment of the hydrochloric acid precipitate with ether, there remains behind a residue amounting to about 10 p.c. of the original resin. This is the *β-resin*. It is soluble in alcohol and acetic acid, but insoluble in ether, benzene, chloroform, and carbon bisulphide (*v.* Herzig, M. 125, 823). Besides a little gum and mineral matter two other constituents have been found in small quantity in guaiacum. One of these is *guaiacic acid* $C_{12}H_{16}O_6$, which occurs only in traces in the resin but in much larger proportion in guaiacum wood (Thierry, J. Ph. 27, 381). It forms colourless needles which sublime unchanged and are soluble in water and alcohol. The other substance is a colouring matter *guaiacum yellow*, first noticed by Pelletier and obtained by Hadelich in pale-yellow octahedral crystals. It is a weak acid, and dissolves in sulphuric acid with a transient blue colour (*v.* Gm. 17, 241 a. 247).

The products of the destructive distillation of guaiacum are very interesting. The lighter portions contain *guaiacene*, *guaiol*, or *tiglic aldehyde* $CH_3.CH{:}C(CH_3).COH$ (Deville, C. R. 17, 1143; 19, 134; Volckel, A. 89, 346), a compound which is also produced by the action of acetaldehyde on propionaldehyde in presence of a dehydrating agent (Lieben a. Zeisel, B. 14, 932). That it behaves as an aldehyde towards acid sulphite of sodium and on oxidation yields tiglic acid was shown by Herzig (M. 3, 119) (*v.* Hlasiwetz, A. 106, 380). Among the heavier products are guaiacol creosol and pyroguaiacin. *Guaiacol* $C_6H_4.OCH_3.OH[1{:}2]$ is the monomethyl ether of orthodihydroxybenzene or catechol (Sobrero, A. 48, 19; Deville a. Pelletier, A. 52, 406; Völckel, A. 89, 346; L. a. Z.; Herzig). This aromatic oil, which boils at 200°, is readily prepared from catechol and methyl-sulphate of potassium (Gorup, A. 147, 248). By the action of nascent carbon monoxide, chloroform, and alkali, it may be converted into vanillin

$$C_6H_4.OCH_3.OH + CO$$
$$= C_6H_3.COH.OCH_3.OH[1{:}3{:}4]$$

(Reimer, B. 9, 424). A carboxylic acid derived from guaiacol has been employed as an antiseptic. It is obtained by the action of carbon dioxide under pressure on the sodium derivative of guaiacol (Ph. [3] 20, 977). Guaiacol itself has been suggested as a substitute for creosote (Sahli, Am. J. Pharm. 1888, 239), also benzoyl-guaiacol (Walzer, Chem. Z. 15, 165). *Creosol* $C_6H_3CH_3.OCH_3.OH[1{:}3{:}4]$ is the monomethyl ether of homocatechol (Hlasiwetz, A. 106, 339). It is a faintly aromatic smelling oil, which boils at 220°, and may be prepared by distilling homovanillic acid with lime (Tiemann a. Nagai, B. 10, 206). *Pyroguaiacin* condenses towards the close of the distillation in pearly crystals. It was investigated by Pelletier and Deville (C. R. 17, 1143), Ebermayer (J. pr. 112, 291), Nachlauer (A. 106, 382) and Hlasiwetz (A. 106, 381; 112, 182). According to Wieser (M. 1, 595), who has recently examined pyroguaiacin, it has the formula $C_{18}H_{18}O_3$. The crystals melt at 180·5°, boil at 258° (80–90 mm.), are nearly insoluble in water and alcohol, and only sparingly soluble in ether. He describes acetyl, benzoyl, and bromine derivatives. When pyroguaiacin is distilled with zinc-dust it yields the hydrocarbon *guaiene* $C_{12}H_{12}$ in the form of brilliant plates which melt at 97–98° and possess a faint blue fluorescence. Wieser obtained two other compounds from pyroguaiacin; the one, *guaiene-quinone*, by oxidising it in acetic acid solution, which gave on analysis the formula $C_{12}H_{10}O_2$, and the other by fusing the hydrocarbon with caustic potash, a compound which melted at 202°, and has probably the formula $C_{12}H_{12}O_2$. When guaiacum itself is melted with potash protocatechuic acid is found among the products (Bötsch, M. 1, 615).

Guaiacum is used in medicine as an alterative in gout, rheumatism, and syphilis.

Hemlock Spruce Resin. *Canada Pitch*; *Pix Canadensis*. (*Poix de Canada*, Fr.; *Canadisches Pech*, Ger.) The hemlock spruce, *Pinus canadensis* (Linn.), yields a reddish-brown resin nearly allied to Burgundy pitch. For botanical characters *v.* Bentl. a. T. 264. Canada pitch consists of *resins* and a trace of *volatile oil*. These have, however, been little investigated. It finds a place in the Pharmacopœia of the United States.

Indian Hemp Resin (*Cannabin*). The common hemp, *Cannabis sativa* (Linn.), when grown in India develops a physiological activity not different in kind, but of greatly increased intensity, to that possessed by the plant in Europe or America. For drawings *v.* Bentl. a. T. 231. *Indian Hemp* (*Cannabis Indica*, B. Ph.; *Chanvre indien*, Fr.; *Indischer Hanf*, Ger.) contains, together with a *volatile oil*, a resin to which the name *cannabin* has been applied, and to which the powerful narcotic properties of the drug are ascribed (Roux, J. Ph. Feb. 1887). This resin was isolated by T. and H. Smith (Ph. 6, 171) as a brown amorphous solid. The method employed for its extraction was essentially treatment of the dry aqueous extract of the herb with alcohol, purification of the alcoholic solution, and precipitation of the resin therefrom by water. Cannabin so obtained possesses narcotic properties in a very high degree. It yields by treatment with nitric acid yellow crystalline *oxycannabin* $C_{20}H_{20}N_2O_7$, which melts at 176°, is insoluble in water and sparingly soluble in alcohol (Bolas a. Francis, C. N. 24, 77). For characters of the volatile oil of Indian hemp *v.* Personne (J. Ph. [3] 31, 46), Martius (C. C. 1856, 25), and Valenta (C. 10, 479; 11, 196).

Among other constituents occurring in small quantities in Indian hemp, nicotine was announced by Preobraschensky (P. Z. 1876, 705), but its presence is denied by Siebold and Bradbury (Ph. [3] 12, 326). The latter, however, find traces of a new volatile alkaloid *cannabinine*, and a similar base has recently been isolated by H. F. Smith (Ph. [3] 22, 267). Another alkaloid tetanocannabine, according to Hay (Ph. [3] 13, 998), exists in the herb; but this is questioned by Warden and Waddell (Ph. [3] 15, 574). Tetanocannabine is possibly identical with *choline*, found by Jahns (Ar. Ph. 25, 479) to be a constituent of Indian hemp.

Jalap Resins. The *true jalap resin* is extracted from the roots of *Ipomœa purga* (Hayne) by alcohol, and, after concentration of the alcoholic solution, precipitated therefrom by water. It is a mixture of two resins: one soluble in ether, *convolvulin*, 5 to 7 p.c., and the other insoluble in ether, *jalapin*, which constitutes the remainder of the resin.

Male or *Orizaba jalap*, the product of *Ipomœa orizabensis* (Ledanois), contains both *jalapin* and *convolvulin*, but the latter in the larger proportion.

Tampico jalap, from *Ipomœa simulans* (Hanbury), consists of *convolvulin* only.

Both jalapin and convolvulin are glucosides; *v.* GLUCOSIDES.

Kamala Resins. Kamala, a fine mobile powder of a dull-red colour, consists of the glands and hairs of the capsules of *Mallotus philippinensis* (Müller, Arg.). The shrub is described by Bentl. a. T. 236. Kamala has long been known as an orange dye-stuff, and more recently as a remedy for the expulsion of tape worm. Kamala, or a drug closely resembling it, is mentioned as early as the tenth century by the Arabian writers. It grows in Abyssinia, Arabia, the East Indies, and Australia. Good kamala yields at least three-quarters of its weight of resin, but it is often largely contaminated with mineral matter. According to Anderson (N. Ed. P. J. 1, 300; J. 1855, 669), who examined kamala in 1855, it contains: resinous colouring matter, 78·19 p.c.; albuminoids, 7·34 p.c.; cellulose, 7·14 p.c.; water, 3·49 p.c.; and ash, 3·84 p.c. *V.* Kirkby (Ph. [3] 14, 897).

Anderson finds that a hot alcoholic extract of kamala deposits on cooling an *amorphous resin* agreeing with the formula $C_{20}H_{31}O_4$, and which is sparingly soluble in cold alcohol and insoluble in water. The clear solution evaporated leaves a *dark-red resin*, which on analysis gives numbers requiring the formula $C_{30}H_{30}O_7$. This resin is soluble in alcohol, insoluble in water, and melts at 100°. Leube (J. 1860, 562) also finds crude kamala resin to consist of two resins which differ somewhat from those described by Anderson. By treating kamala with ether, Anderson observed that the solution obtained, on standing, gave an abundant crystalline precipitate of a substance which he called *rottlerin* $C_{11}H_{10}O_3$. This compound is insoluble in water, sparingly soluble in cold, but readily in hot alcohol, and is soluble in ether. The existence of this body is confirmed by A. G. and W. H. Perkin (B. 19, 3109), who prepare it by the use of carbon bisulphide instead of ether, and call it 'mallotoxin.' They describe an acetyl derivative ($C_{11}H_8O_3(C_2H_3O)_2$ or $C_{11}H_7O_3(C_2H_3O)_3$. Jawein (B. 20, 182) obtains similar results. For substitutes for kamala *v.* *Wars* or *Waras resin.*

Kosin Resin (*Koussin*). The female flowers of *Hagenia abyssinica* (Willd.), a tree which grows in the higher districts of Abyssinia, contain a crystalline resin, *kosin*. Wittstein (R. P. 71, 25) examined koso in 1840, and found the flowers to contain 6 p.c. of an acrid bitter resin, together with wax gum, and one-fourth of their weight of tannin. Kosin was further studied by Pavesi (J. 1859, 585) and by Bedall (J. 1862, 513). To obtain it the drug is mixed with lime, and extracted first with alcohol and afterwards with water. The solutions are mixed together and concentrated. Acetic acid is then added, which liberates the kosin from its soluble calcium salt, when it slowly precipitates.

Commercial kosin was examined by Flückiger and Buri (J. 1874, 900; Fl. a. H. 258), who found it to consist essentially of yellow rhombic crystals, which melt at 142°, and have the composition $C_{31}H_{38}O_{10}$. The crystals are insoluble in water, but easily soluble in alcohol, ether, benzene, glacial acetic acid and in alkalis. Ferric chloride gives a red colour with an alcoholic solution of kosin. An acetyl derivative was prepared (*v.* Liotard, J. Ph. 1888, 507).

Koso is employed in medicine as a vermifuge.

Lac Resin. *Gum Lac; Lacca.* (*Laque*, Fr.; *Lack*, Ger.) Lac is an exudation produced by the puncture of the hemipterous insect, *Coccus lacca* (Kerr), on the young branches of many East Indian lacticiferous trees. The resin exudes and dries on the branch, covering it and imbedding the insects and protecting their eggs. The female insect contains a red colouring matter. The small branches covered with resin are known in commerce as *stick lac.* When the resin is removed it is called *seed* or *grain lac*, and when melted by boiling with water and cooled in thin layers it becomes *shellac.* The water in which seed or stick lac has been boiled contains the colouring matter, which on evaporation constitutes *lac dye.* Shellac is bleached by treatment with sulphurous acid or chlorine. It is soluble in alcohol, alkalis, and in hydrochloric and acetic acids. It consists of a mixture of resins, together with small quantities of wax, fat, and extractive matter (von Esenbeck a. Marquart, A. 13, 286; Benedikt a. Ehrlich, M. 9, 158; Benedikt a. Ulzer, M. 9, 580; also Gm. 17, 419). It is used for varnishes, and is the basis of the better kinds of sealing-wax. A liquid shellac is prepared by the action of hot alkalis (B. a. E.).

Lac dye was examined by Schmidt (B. 20, 1287), who finds it to contain a crystalline compound *laccaic acid*, $C_{16}H_{12}O_8$ (?), the salts of which possess the characteristic red colour of the dye. The acid resembles carminic acid.

Lanoresin. A resin or gum-resin obtained from the washings of wool (S. C. I. 1890, 1046).

Masopin Resin. A resinous substance obtained from the Dschilte tree, and used in Mexico for chewing. It is a snow-white powder, without taste or smell, insoluble in water but soluble in alcohol or ether. From an ethereal solution crystals may be obtained. These melt at 155°, but in melting undergo a change by which the melting-point falls to 70°. Masopin has the composition $C_{22}H_{36}O$ (Genth, A. 46, 124).

Mastich Resin. *Mastiche.* (*Mastic*, Fr.; *Mastiq*, Ger.) Mastich is the concrete resinous exudation of *Pistacia Lentiscus* (Linn.), an evergreen shrub inhabiting the shores of the Mediterranean (Bentl. a. T. 242). It comes chiefly from the island of Scio. Mastich has been known from ancient times, but it is employed less and less in pharmacy, and is being replaced by other resins in the manufacture of the finer varnishes. An effort is, however, being made to develop the mastich production in Scio (S. C. I. 1889, 583 a. 656). It occurs in 'tears,' or in masses of a pale-yellow colour; is brittle, and has a faint balsamic odour. It softens in the mouth, and melts at about 108°. Warm acetone dissolves mastich freely. Alcohol separates it into two resins, the *α-resin*, constituting 90 p.c. of the original mastich, dissolves, while the *β-resin* remains insoluble. Mastich contains a trace of volatile oil. The (*α*) resin appears to be an acid, and was analysed by Johnston (Tr. 1839, 132). According to Hartsen (B. 9, 316), it may be obtained in crystals. The volatile oil, which in some specimens amounts to 2 p.c., was examined by Flückiger (Ar. Ph. [3] 19, 170). It boils at 155 to 160°, and consists essentially of a *terpene* $C_{10}H_{16}$, possessing a strong but agreeable odour (*v.* Gm. 17, 423; Fl. a. H. 161).

Maynas Resin (*Calaba, Galba*). A resin extracted by incision from the tree *Calophyllum Calaba* (Jacq.) which inhabits the plains of San Martino and the Orinoco. When purified by solution in alcohol it crystallises in prisms. It is soluble in alcohol, ether, alkalis, and in acetic and sulphuric acids. Analysis led to the formula $C_{14}H_{18}O_4$ (Lewy, A. Ch. [3] 10, 380).

Mezereon Resin. The acrid constituent of mezereon bark is a resin. The bark is obtained from the shrubs of *Daphne Mezereon* (Linn.) and other species of daphne. These shrubs, with their red, fragrant flower-clusters preceding the leaves, inhabit southern and middle Europe, and grow in England as far north as Yorkshire (*v.* Bent. a. T. 225-227).

Mezereon *resin* has not been recently examined. It was prepared by Gmelin (Schw. J. 35, 11) and by others (Gm. 17, 176), and, according to Zwenger (A. 115, 17), it yields, on distillation, umbelliferone. Vauquelin (A. Ch. 84, 174), also Gmelin and Baer (Schw. J. 35, 1), isolated from various species of daphne a crystallisable compound daphnin. This was shown to be a glucoside by Zwenger (A. 115, 1). It breaks up by the action of acids into glucose and *daphnetin*. Daphnetin has been synthesised by Pechmann (B. 17, 929), and its constitution has been further studied by Will and Jung (B. 17, 1081) and by Jung (C. C. 1886, 41). Among the other constituents of mezereon is a *vesicating fatty oil*, which occurs chiefly in the fruit (Martius, Ar. Ph. [2] 110, 39).

In medicine mezereon is employed as an alterative in rheumatism and scrofula, and is sometimes used as a vesicant.

Norway Spruce Resin. *Burgundy Pitch*; *Pix Burgundica*. (*Poix de Bourgogne*, Fr.; *Fichten* or *Tannenharz*, Ger.) Burgundy pitch is the prepared resin of *Pinus abies* (Linn.), the Norway spruce fir. For drawing *v.* Bentl. a. T. 261. The market is supplied with Burgundy pitch chiefly from the Grand Duchy of Baden, Austria, and Switzerland. The ordinary method of collection is to make incisions, and to allow the oleoresinous juice which exudes to harden on the trees. It is then removed and treated with boiling water, whereby a resin practically free from volatile oil is obtained. Burgundy pitch resembles colophony, and probably consists for the most part of the anhydride of abietic acid. It is employed in medicine for plasters. When colophony is melted and mixed with a little fat and water, and stirred as it cools until it solidifies, a mixture is obtained which has the opacity and other characters of Burgundy pitch, and is largely substituted for the true resin.

Palm-Wax Resin (*Ceroxylin*). Palm-wax, the product of *Ceroxylon andicola*, a palm of New Granada, contains a resin. It may be separated from the wax by solution in alcohol. It melts above 100°, and is said to have the composition $C_{20}H_{32}O$ (Boussingault, A. Ch. 29, 330; 59, 19).

Pellitory Resin. The root of *Anacyclus Pyrethrum* (De Cand.), 'pellitory of Spain,' has long been known as a powerful local irritant and sialogogue. It comes for the most part from Algeria. A drawing of the plant is given by Bentl. a. T. 151. The acrid properties of the root seem to depend upon its resinous constituent, *pyrethrin* (Gaultier a. Parisol, J. Ph. 1818, 49; 1834, 251; Köne, A. Ch. [2] 59, 328). Thompson (Ph. [3] 17, 567) prepares the resin as follows: The root is powdered and percolated with alcohol. The residue is then acidulated with acetic acid and extracted by boiling alcohol. Finally the two liquids are mixed together and evaporated. Thus obtained, pyrethrin is a mixture of an acid-brown resin with some, probably inactive, fixed oil. Pellitory contains, besides pyrethrin, *fixed oil*, *gum*, *inulin*, a trace of tannin, and, according to Buchheim (Ph. [3] 7, 315), a compound *pyrethrine*, analogous to piperine, which, by the action of caustic alkalis, takes up the elements of water and breaks up into *piperidine* and *pyrethric* acid.

Similar resinous constituents are found in the root of German pellitory, *A. officinarum* (Hayne) (Bentl. a. T. 152; Fl. a. H. 384).

Pepper Resin. Pepper appears in commerce as 'black,' 'white,' and 'long' pepper. The black and white varieties are the dried fruit of the same plant, the white appearance being due to the removal of the dark-coloured pericarp. Both are obtained from *Piper nigrum* (Linn.) a climbing shrub, indigenous to Travancore and Malabar, and cultivated largely in both the East and West Indies. Long pepper consists of the dried spikes of the minute fruits of *Piper officinarum* (De Cand.), a shrub inhabiting the Indian Archipelago (*v.* Bentl. a. T. 244-245). Pepper has been known from the earliest times. Theophrastus was acquainted with black and long pepper, and white pepper is mentioned by Dioscorides. The Romans levied duty on black pepper in Alexandria, A.D. 176 (Fl. a. H. 577).

The pungent taste of pepper is due to its *resin*, but this has not been studied chemically. Pepper contains 1 to 2 p.c. of a *volatile oil*, upon which its odour depends. The volatile oil was examined by Dumas (A. 15, 159) and by Soubeiran and Capitaine (A. 34, 327). It consists essentially of a terpene boiling at 164 to 165°, and having the specific gravity of 0·873 (15°) (Eberhardt, Ar. Ph. [3] 25, 515). The most interesting constituent, however, is the crystalline base *piperine* $(C_5H_{10}N)C_{12}H_9O_3$, discovered by Oersted in 1819 (Schw. J. 29, 80). It was further investigated by Pelletier (A. Ch. [2] 16, 344; 51, 199) and others, and Stenhouse found it to be a constituent of cubebs (A. 95, 106). Pepper contains from 5 to 15 p.c. of this compound. By the action of alcoholic potash it breaks up into the alkaloid *piperidine* $C_5H_{11}N$, and *piperic acid* $C_{12}H_{10}O_4$. Piperidine may be obtained, as Ladenburg has shown (B. 17, 513), by the action of nascent hydrogen on pyridine. It is, therefore, probably hexahydropyridine. A recent examination of pepper by Johnston (C. N. 58, 235; An. 14, 41) shows that this alkaloid exists ready formed in the spice to the extent of from 0·2 to 0·8 p.c. According to Buchheim, pepper contains another compound, *chavicin*, which by the action of alkalis yields *chavicic acid* and piperidin (Ph. [3] 7, 315).

Pepper is used extensively as a spice. When ground it is liable to adulteration, chiefly with starch and serials. Such admixture is mostly detected by microscopical examination. See Hassall ('Food Adulteration,' 2nd ed. 356); Blyth ('Foods: their Composition and Analysis,' 492). For analysis of peppers of commerce *v.* Johnston (An. 14, 41).

Podophyllum Resin. *Resina podophylli.* (*Résine de podophylle*, Fr.; *Podophyllumharz*, Ger.) This favourite purgative is obtained from the rhizome and rootlets of May apple, *Podophyllum peltatum* (Linn.), which, with its beautiful wax-like flower, grows abundantly throughout the American continent, east of the Mississippi and south of Hudson's Bay (Bentl. a. T. 17). It is also said to occur in Japan (Ph. [3] 19, 346). Only two species of the genus *Podophyllum* are known. The second, which yields the Indian podophyllum, *P. Emodi* (Wallich), possesses the same properties as the American species. It inhabits the shady valleys of the Himalayas, and is abundant in Kunawin and Kashmir (Dymock a. Hooper, Ph. [3] 19, 585).

Besides the *resin*, upon which the purgative property of the drug depends, Mayer, who examined podophyllum in 1863 (Am. J. Pharm. 1863, 97), reported it to contain berberine, saponin, and a colourless alkaloid; but no evidence of these compounds, at least in the crude resin, has been obtained by subsequent observers (Power, Am. J. Pharm. 1878, 369; Maisch, Am. J. Pharm. 1879, 590; Biddle, Ph. [3] 10, 468).

The resin is prepared by extracting the dried and powdered drug with alcohol, and throwing the alcoholic solution into water or water acidulated with hydrochloric acid, the latter helping the resin to agglomerate, and thus to subside more readily. The precipitate should be dried by simple exposure to the air, or, at all events, at temperatures below 35°. Thus prepared, podophyllum resin has a greyish-white, slightly yellow, or greenish-yellow colour. If higher temperatures be employed the resin is darker. A more distinct yellow colour is produced by the use of alum water as a precipitant. Variations in colour, observable in commercial specimens, have not been found to affect appreciably their physiological activity (Senier a. Lowe, Ph. [3] 8, 443; Klie, Am. J. Pharm. 1877, 578; Busch, Am. J. Pharm. 1877, 548; Lloyd, Ph. [3] 10, 70; Jones, Chem. Drug. 34, 701). The yield of resin varies from 3 to 5 p.c. From Indian podophyllum 12 p.c. of crude resin was obtained by Dymock and Hooper.

Podophyllum resin is soluble in alcohol and caustic alkalis. From its alkaline solution it is re-precipitated by acids. Although the resin is precipitated from its alcoholic solution by water, it is not insoluble in that menstruum. As much as 80 p.c. may be dissolved in hot water, and only a part of this re-precipitates on cooling. Power finds the crude resin to melt at 120 to 124°. Ether dissolves about 60 p.c. of the resin (*v.* Guareschi, G. 10, 16).

The investigations of Podwyssotzki have thrown much new light on the chemistry of podophyllum (Arch. Path. u. Pharm. 13, 29; P. Z. 20, 49; 140, 208 a. 777; Ph. [3] 12, 217 a. 1011). The author reviews experimentally the literature of podophyllum, and isolates a series of definite crystalline and other constituents, the properties of which he has studied, and to one of which he finds the medicinal activity to be due. These compounds exist both in podophyllum and in the resin, but they are more readily obtained from the crude drug. The essential constituent is a colourless, amorphous, poisonous bitter, *podophyllotoxin*, which, by the action of lime-water, splits into a neutral, crystalline, bitter, poisonous *picropodophyllin*, and the calcium salt of inactive *picropodophyllic acid.* The colour of podophyllum is due to the compound *podophylloquercetin*, which crystallises in yellow needles with a metallic lustre. The other constituents are inert *podophyllic acid* and an inactive *resin insoluble in ether.* The active purgative constituent is picropodophyllin.

To obtain podophyllotoxin podophyllum is extracted with cold chloroform, which must be free from alcohol, otherwise podophylloquercetin is dissolved also. The chloroformic solution concentrated to a syrup is poured into ether, when inert podophyllic acid, insoluble in ether, is precipitated. If the clear liquid is now dropped into petroleum ether this solvent retains the fat, and the podophyllotoxin is precipitated as a white powder. It may be purified by re-solution in chloroform and repetition of this process. Thus obtained, podophyllotoxin is a very bitter white or pale-yellow powder, and dissolves in weak spirit or in hot water. It is readily soluble in chloroform or ether, but it is insoluble in petroleum ether. Analysis gave C 67·62 p.c., H 7·46 p.c., O 24·92 p.c. Podophyllotoxin may be administered to adults in doses of $\frac{1}{4}$ to $\frac{1}{2}$ grain in alcoholic solution.

Picropodophyllin is prepared from podophyllotoxin by mixing the alcoholic solution with slaked lime and evaporating to dryness on a water-bath. The residue extracted with hot absolute alcohol yields silky crystals of picropodophyllin on cooling. This compound possesses the activity of the drug in the highest degree. A dose of 4 centigrams administered to a cat caused death, preceded by violent evacuations and vomiting. It is very soluble in chloroform or alcohol, but insoluble in water or petroleum ether. On burning it gave C 67·71 p.c., H 5·31 p.c., O 26·98 p.c. The resinous compound, picropodophyllic acid, may be prepared from the residue, after extraction of picropodophyllin, in which it exists in combination with calcium. It has no physiological activity, and was not obtained in a sufficiently pure state for analysis. After podophyllum has been treated with chloroform as described, and with petroleum ether to remove fat, the podophylloquercetin, which is insoluble in these solvents, is extracted by ether. The ethereal solution is evaporated, and the podophylloquercetin purified by conversion into a lead compound, and subsequent regeneration and re-solution in ether. After removal of the ether it remains as a yellow powder, which may be obtained in yellow crystals by sublimation. On exposure to the air it changes to green, a fact which accounts for some of the colours observable in the commercial resin. It has no emetic or aperient action, but is, perhaps, the cause of the intestinal pain which sometimes accompanies the administration of podophyllum. Podophylloquercetin is the colouring agent of podophyllum. It is insoluble in water, and forms with alkalis bright-yellow solutions. Ferric chloride colours it dark green. It melts at 247–250°, and on analysis gives C 59·37 p.c., H 4·01 p.c., O 36·62 p.c.

The investigations of Podwyssotzki have recently been supplemented to an important extent by Kürsten (Ar. Ph. 229, 220). By a slightly modified process the constituents discovered by the former chemist have all been obtained in crystals and have been analysed. Podophyllotoxin forms prisms melting at 93–95° and having the composition $C_{23}H_{24}O_9,2H_2O$. With sulphuric acid it gives a cherry-red colour, changing to greenish-blue and violet. It does not appear to contain hydroxyl, but by Zeisel's method gives evidence of the presence of three methoxyl groups. Oxidised by permanganate in alkaline solution it yields podophyllic acid, $C_{20}H_{24}O_9$, in well-formed crystals. This acid melts at 158–160° and forms a copper salt, $C_{20}H_{23}O_9Cu$, consisting of light-green prisms. The crystalline picropodophyllin obtained by the action of alkalis on podophyllotoxin proves to be an isomeride of that compound. It yields the same products when oxidised, but melts at 227°. Picropodophyllic acid, which was obtained in small quantity, forms crystals which melt at 156–158°. It closely resembles podophyllic acid, $C_{20}H_{24}O_9$. Crystalline podophylloquercetin, $C_{23}H_{16}O_{10}$, melts at 275–277°. It may possibly prove to be quercetin.

Kremel (Ph. Post, 1889, 105) suggests that podophyllum resin should be valued by a determination of the proportion of podophyllotoxin which it contains. About a gram of the resin is treated with chloroform in the cold as long as anything is dissolved; the solution obtained is evaporated to a small bulk, and then poured into twenty times its volume of petroleum ether. The podophyllotoxin separates, and is collected, dried, and weighed. Commercial specimens of resin yield 20 to 30 p.c.

Rhubarb Resin (*v.* RHUBARB).

Sandarac. *Sandaraca.* (*Sandaraque*, Fr.; *Sandarak*, Ger.) A pale-yellow translucent exudate from a small evergreen tree, *Callitris quadrivalvis* (Ventenat), which inhabits North-western Africa. It somewhat resembles mastich, but is brittle between the teeth. The investigations of Unverdorben (Scher. J. 60, 82) and Johnston (Tr. 1839, 293) show that it contains three resins. From an alcoholic solution of the crude resin, alcoholic potash precipitates the (γ)-*resin* in combination with potassium. When purified and set free by an acid the (γ)-resin is a difficultly-fusible white powder. It is the 'sandaracin' of Geise (Scher. J. 9, 536). The alcoholic mother-liquor from the separated (γ)-resin contains the (α)- and (β)-*resins*, which may be separated by 60 p.c. alcohol, in which the (α)-resin is easily, and the (β)-resin difficultly soluble. Sandarac, which is also known in commerce as 'gum juniper,' is used in the preparation of varnishes.

For Australian and Tasmanian sandarac *v.* Maiden (Ph. [3] 20, 562).

Wars or Waras Resin. This drug, which, coming from India or Arabia, has from time to time appeared as a substitute for kamala, consists of the glands and hairs of species of *Flemingia.* The powder resembles kamala, but is of a darker colour. It yields resin to the same extent as kamala, and is closely related to that drug in all its characters. *V.* Flückiger (Ph. [2] 9, 279; [3] 17, 1029; 18, 110), Kirkby (Ph. [3] 14, 897), Dyer (Ph. [3] 14, 917 a. 969) and Hooper (Ph. [3] 18, 213). A. S.

RESINATE LAKES. These lakes are prepared by dissolving 100 parts of pale-coloured resin in a solution of 33 parts of soda crystals in 1,000 parts of water. The mixture is boiled for an hour, after which it is cooled down to about 50°C. by the addition of 1,000 parts of cold water, and then the filtered solutions of such basic dyes as magenta, methyl-violet, brilliant green, auramine, &c., are added. The amount of dye used depends on the depth of colour desired, and varies between 5 and 15 p.c. on the amount of resin. The resin-soap solution must be of the right temperature and degree of concentration when the addition of dye is made, so as to avoid the separation of the colour bases in the form of resinates. A slight excess of a dilute solution of a metallic salt is added; in the case of zinc sulphate, 55 parts dissolved in 1,000 parts of water are used for the above quantities of resin, &c. The solutions of magnesium salts must be very dilute, since otherwise the lake becomes resinous on drying. The lakes which are not to be used in the paste form are thoroughly dried at a temperature of 40° to 50°, or 70° in the case of magnesium lakes. The dried lakes are of an exceedingly fine bright colour. They are not affected by air or moisture, and boiling water fails to extract colouring matter. Weak alkalis and acids are also without action, and strong solutions of hypochlorites act very slowly on them, provided that light is excluded; but, in presence of light, oxidising agents act rapidly. Their solubility in alcohol depends upon the nature of the combined metallic base; magnesium lakes dissolve easily, calcium and barium lakes fairly easily, aluminium and iron lakes only slightly. Benzene, ether, chloroform, light petroleum, and other solvents dissolve them easily. Some of the lakes—those of aluminium, for instance—are decomposed when their solutions are kept for a little time, the metallic base separating, but others, such as those of zinc and calcium, keep indefinitely. They resist light fairly well. Lakes made with brilliant green resist badly, but those coloured with auramine, methyl-violet, saffranine, chrysoidine, and particularly rhodamine, resist very well. The colours bleach more easily when in combination with aluminium and chromium than with zinc and magnesium. The action of light renders the lakes insoluble in benzene, liberating the colour-base, which may be extracted with hot water. The solutions of the lakes form good varnishes, whose elasticity and power of endurance are increased by the addition of a little indiarubber or guttapercha. The following is an example of such a varnish: 30 parts of magnesium lake are dissolved in 80 parts of benzene and 20 parts of chloroform, and the solution obtained mixed with 150 parts of a clear solution of $1\frac{1}{2}$ p.c. of indiarubber in chloroform and benzene (A. Müller-Jacobs, D. P. J. 273, 139–142; S. C. I. 8, 770).

RESOIN *v.* Phenol and its homologues.

RESOPHTHALIN. *Fluorescein v.* Triphenyl methane colouring matters.

RESORCIN. *Resorcinol v.* Phenol and its homologues.

RESORCIN BLUE *v.* Phenol colouring matters.

RESORCIN BROWN. The sodium salt of xylidin-azo-sulphanilic-azo-resorcin. A brown powder, soluble in water and sulphuric acid, forming brown solution. Dyes wool brown in an acid bath.

RESORCIN YELLOW *v.* Azo- colouring matters.

RESORUFIN *v.* Phenol colouring matters.

RETENE or **METHYL-PROPYL-PHENANTHRENE** $C_{18}H_{18}$ (Bamberger and Hooker), occurs in high boiling tar oils derived from resinous pine-wood, and forms a faintly yellow, glittering, crystalline powder, which melts to a yellow oil at 98·5°. It can be melted together with different oils, fats, and hydrocarbons, and raises or lowers their melting-point accordingly. It can also be obtained by distilling resin oil with sulphur. The fossil resin of the coniferæ, as found in Switzerland, Bavaria, and Denmark, contains retene as its principal constituent. It appears, indeed, very probable that the hydrocarbon is in every case derived from the coniferæ; *v.* Ekstrand, A. 185, 75; E. v. Boyen, C. Z. 11, 1,297; S. C. I. 7, 116.

RETIN ASPHALT *v.* Resins.

RETINIC ACID *v.* Resins.

RETINITE *v.* Resins.

RHAMNETIN *v.* Persian-berries.

RHAMNOSE (*Isodulcite*) $C_6H_{12}O_5 + H_2O$ (*cf. Persian-berries*, p. 128). Rhamnose appears to be fairly widely distributed in nature in the form of glucosides, the following of which class of substances yield it on hydrolysis: xanthorhamnin (Liebermann and Hörmann), quercetrin (Liebermann and Hamburger, B. 12, 1178), rutin (Schunck, C. J. 1888, 263), sophorin, the colouring matter of so-called Chinese yellow berries, which are really the unexpanded flower buds of *Sophora japonica* (Foerster, B. 15, 215), hesperidin (Tanret, Bl. 49, 23) and frangulin (Thorpe and Miller, C. J. 1892).

Its empirical formula $C_6H_{14}O_6$ formerly led to its being classed with dulcitol and mannitol, but Fischer and Tafel showed that its behaviour with phenyl-hydrazine and with Fehling's solution distinguished it from the hexatomic alcohols, and indicated it to be an aldehyde or ketonic alcohol of the composition $C_6H_{12}O_5$, and which unites with a molecule of water in the same way as certain other aldehydes—as, for example, choral and glyoxylic acids. It yields an osazone $C_6H_{10}O_3(N_2H.C_6H_5)_2$ melting at 180°, and a phenylhydrazone $C_6H_{12}O_4.N_2H.C_6H_5$ which melts at 159°. The same chemists also prepared rhamnosecarboxylic acid, and submitted this to the action of hydrogen iodide, when a lactone and *normal heptylic acid* were produced. The formation of the latter proved that rhamnose contains a normal carbon chain and an aldehyde grouping. These facts together with Herzig's observation that acetic acid is formed on oxidising rhamnose with silver oxide, and from which he concluded that rhamnose contains a methyl group, rendered it highly probable that the sugar in question has the constitution

$$CH_3.CHOH.CHOH.CHOH.CHOH.COH,$$

that it is, in fact, methylarabinose. The correctness of this view was finally proved by Maquenne, who showed that rhamnose undergoes the same decomposition as arabinose when distilled with sulphuric acid, that whilst arabinose yields its anhydro- derivative furfuraldehyde, rhamnose gives the homologue of this methylfurfuraldehyde. The latter must therefore be regarded as an anhydro- derivative of rhamnose.

The following references may be given in addition to those found under Persian-berries: Fischer and Tafel, B. 20, 1,091, 2,574; 21, 1,657, 2,173; Fischer, B. 22, 96; Fischer and Passmore, B. 22, 2,733; Maquenne, C. R. 109, 603; Raymann and Kruis, Bl. 47, 668, 760; 48, 632; Raymann, B. 21, 2,046; Will and Peters, B. 21, 1,813; 22, 1,697.

RHATANY ROOT. The dried root of *Krameria triandra* (Peruvian rhatany) or *K. Ixina* (Savanilla rhatany). The bark contains about 20 p.c. of a kind of tannin. Is a strong astringent. For rhatany red *v.* Grabowski, A. 143, 274.

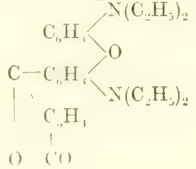
RHEIC ACID *v.* Rhubarb.

RHEOTANNIC ACID *v.* Rhubarb.

RHINANTHIN $C_{29}H_{52}O_{20}$. A glucoside found in the seeds of *Alectrolophus hirsutus* and *Rhinanthus crista-galli*, or yellow rattle, and which gives rise to the violet colour occasionally found in rye bread (Ludwig, Z. [2] 5, 303; Ar. Ph. [2] 142, 199). It has a nauseously bitter-sweet taste, and crystallises in prisms.

RHOCADINE *v.* Vegeto-alkaloids.

RHODAMINE. The first representative of an interesting class of dyes obtained by fusing the amido-phenols or their derivatives with phthalic anhydride. Rhodamine is formed by heating together 1 mol. of phthalic anhydride with 2 mols. of diethyl-meta-amidophenol $C_6H_4\left\{N(C_2H_5)_2\right\}OH$, for several hours at 200°. The constitution of the pure product obtained is



a body in which the basic properties evidently predominate. The commercial product is the hydrochloride. It is obtained as a brown-red powder, easily soluble in water, with a fine crimson colour and a characteristic orange fluorescence. The scarlet fluorescence of the glacial acetic acid solution is very fine. On heating the aqueous or acetic acid solution to about 90°, the fluorescence vanishes, but reappears on cooling. Tannic acid produces in presence of sodium acetate a bright crimson precipitate (rhodamine tannate), which is not fast to light. The triple compound, however, of rhodamine, tannic acid, and antimony, produced by adding tannic acid to a solution of rhodamine and tartar emetic exposed along with the tannate, was found to resist the action of light very well. With stannous chloride the aqueous solution shows a most characteristic reaction; a cinnabar-red precipitate is produced which, whilst still in a fine state of division, transmits a bright-blue light. In strong sulphuric acid, rhodamine dissolves with a yellow colour, which, on dilution with water, gives place to red again. To wool and silk rhodamine is best applied in a neutral bath, but it can also be dyed in an acid bath, and can, therefore, be employed along with some of the acid dyes. The colours obtained are various shades of pink, which show a marked orange fluorescence. The shades stand light better than those produced by any strong coal-tar colour (with the exception, perhaps, of Magdala red). They also stand soaping fairly well (wool), but when milled strongly are liable to blend into the white.

On cotton, rhodamine is best applied with the tannic acid and tartar-emetic mordant. It may also be fixed on cotton mordanted with Turkey-red oil; in this case the colours obtained are fluorescent (E. Knecht, Jour. Soc. Dyers and Colourists; S. C. I. 7, 560).

RHODIENE. A hydrocarbon $nC_{10}H_{16}$ obtained from rosewood oil (Gladstone, C. J. [2] 10, 3).

RHODIUM *v.* Platinum metals.

RHODOCROISITE. *Manganese carbonate v.* Manganese.

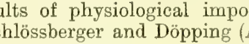
RHODONITE. *Manganese silicate v.* Manganese.

RHŒADINE $C_{21}H_{21}NO_6$. An alkaloid found by Hesse (A. 140, 145; 149, 35) in the red poppy and in the ripe seed-capsules of the white poppy. By the action of dilute mineral acids is converted into the isomeric base *rhœagenine.*

RHUBARB (*Rheum*; *Rhubarbe*, Fr.; *Rhabarber*, Ger.). The root of *Rheum palmatum* (Linn.), *Rheum officinale* (Baillon), and possibly other allied species, all inhabitants of Central Asia. For botanical characters *v.* Bentl. a. T. 213, 214; Fl. a. H. 491; Pereira (Mat. Med. 1850, 2, 1343); also Flückiger (N. R. P. 25, 1), and Baillon (Ph. [3] 3, 301). Attempts have been made from time to time to cultivate the official rhubarb plants in Europe which have been attended with a certain amount of success. Other allied species have also been grown. These have supplied the market with substitutes for the Chinese drug. The most important are *R. Rhaponticum* (Linn.), cultivated for a century in the neighbourhood of Banbury, and the same species, together with *R. palmatum* (Linn.), *R. undulatum* (Linn.), and *R. compactum* (Linn.), which are grown in France and Germany. The comparative value of English rhubarb has been studied by H. Senier (Ph. [3] 8, 444) and Elborne [3] 15, 136).

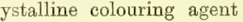
Rhubarb has been known from the very earliest times as a mild purgative and stomachic. Not only was its value appreciated by Dioscorides, but in China its history goes back to the reign of the Emperor Shen-Nung, B.C. 2700. With the advent of chemical inquiry at the beginning of this century the composition of rhubarb was studied by numerous investigators. Of their results a summary is given by Pereira (Mat. Med., 1850, 2, 1355), but, with the exception of the identification of constituents which are common to most plants, this early work only resulted in the preparation of active but chemically indefinite extractives.

The first chemical investigation to give definite results of physiological importance was that of Schlössberger and Döpping (A. 50, 213). These observers isolated *chrysophanic acid*, a yellow crystalline colouring agent which had already been found in the wall-lichen by Rochleder and Heldt (A. 48, 12), and which Liebermann (A. 183, 145) has recently shown to be a derivative of anthraquinone. Chrysophanic acid has also been obtained from *Squamaria elegans* (Thomson, A. 53, 260), *Rumex obtusifolius* (Linn.) (Thann, A. 107, 324), and from senna, *Cassia acutifolia* (Delile), and *C. angustifolia* (Vahl). De la Rue and Müller (C. S. Mem. 10, 298) discovered another crystalline colouring matter of a darker red-orange colour, *emodin.* This compound has also been found in the bark of *Rhamnus Purshiana* (De Cand.), *Cascara Sagrada*, and of *Rhamnus Frangula* (Linn.), and its constitution, according to Liebermann, is, like chrysophanic acid, that of an anthraquinone derivative. Chrysophanic acid is methyldihydroxyanthraquinone



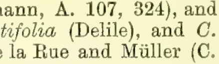
$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H(CH_3)2OH$$

and emodin is methyltrihydroxyanthraquinone



$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6(CH_3)3OH.$$

Both these compounds are therefore nearly related to alizarin, which is a dihydroxyanthraquinone



$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_22OH.$$

Just as in madder alizarin does not occur ready formed, but is the product of the fermentation of a glucoside, so, according to Kubly (P. Z. 6, 603; 24, 193; Ph. [3] 16, 65) chrysophanic acid does not exist to any appreciable extent in rhubarb root, but is produced by the fermentation, in presence of water, of a glucoside *chrysophan.* This view is confirmed by Dragendorff (Ph. [3] 8, 826).

Three somewhat indefinite resinous constituents were isolated, besides chrysophanic acid, from rhubarb, by Schlössberger and Döpping. They are: *aporetin, phæoretin,* and *erythroretin* (*v.* Gm. 16, 176).

Kubly, working in a different way, obtained from rhubarb another series of compounds. This chemist treats an aqueous extract of rhubarb with alcohol, and precipitates the solution obtained with lead acetate. The precipitate, after decomposition with sulphuretted hydrogen, yields to water a yellow-brown pulverulent compound *rheotannic acid* $C_{26}H_{26}O_{14}$. This compound is insoluble in ether but soluble in water and alcohol, and forms a lead salt $C_{26}H_{26}O_{11}2PbO$. By the action of dilute acids it breaks up into fermentable *sugar* and a new substance *rheic acid*, $C_{20}H_{16}O_9$. From the residue after the removal of rheotannic acid by water, alcohol extracts phœoretin, $C_{16}H_{16}O_7$, agreeing in all respects with the description of Schlössberger and Döpping. The filtrate from the original precipitate with lead acetate is decomposed by sulphuretted hydrogen, and the precipitate obtained after removing sugar by treatment with water yields to alcohol an indifferent *colourless crystalline substance* $C_5H_6O_2$, and chrysophan, which, unlike chrysophanic acid, is insoluble in ether and petroleum ether.

For analyses of rhubarb see Dragendorff (Ph. [3] 8, 826), H. G. Greenish (Ph. [3] 9, 933), Elborne (Ph. [3] 15, 137), Dessaignes (J. Ph. [3] 25, 23), and for inorganic constituents Brandes (J. 1853, 581), Tip (J. 1854, 657), and Boni (Ph. Post, 1888, 51). For rhubarb-testing see Maisch (Am. J. Pharm. 43, 259), Howie (Trans. Brit. Pharm. Conf. 1873, 562), Husson (Union Pharm. 16, 99) and H. G. Greenish (Ph. [3] 9, 813). A. S.

RHUBARB RESIN *v.* RHUBARB.

RHYACOLITE *v.* FELSPAR.

RICE is the grain of *Oryza sativa*, a native of Asia, where it is very extensively cultivated in India, Japan, and China. It is also grown in the West Indies, Central America, and the United States.

Crawfurd, reasoning on philological grounds, concluded that rice was introduced into Persia from Southern India. The Arabs carried it into Spain under the name of *aruz*, whence the *arros* of Spanish, *rizo* of Italian, and English *rice*.

The plant itself sports into many varieties, of which Roxburgh enumerated over fifty; some growing in marshy and other in dry ground, some coming to maturity in three months and other at longer periods up to six months. Kellner and Sawano, examining Japanese rice, distinguished mountain rice and marsh rice, the former of which thrives on dry soil and perishes when sown in the wet rice valleys where the second flourishes to die in its turn if sown on dry soil. The two classes are morphologically the same, and the cause of this great difference is as yet undiscovered.

Rice affords food for millions of human beings in tropical climates, but is not equally suitable to temperate countries; the fatty matter contained in it being less than that of other cereals. The amount of gluten in rice, according to Payen's determination, is only 7 p.c., against 22 p.c. in finest wheat flour, 14 p.c. in oats, and 12 p.c. in maize. The percentage of potash is as 18 to 23 in wheat. Rice is also used to an enormous extent for its starch, of which the granules are the smallest among all commercial starches. Rice furthermore is used by distillers.

A section of the grain shows (1) an outer fibrous husk, (2) a layer of gluten cells, and (3) the starch cells. The starch is polygonal, mostly five- or six-sided, here and there three-sided. With a microscope of high power a starred pilum is seen. The average size of the granules is, according to Blyth, from ·0050 to ·0076 mm. (·0002 to ·0003 inch), the maximum, according to Wiesner, being ·022 mm. (·0008 inch).

The following analyses of Carolina and Piedmont rice are by Braconnot:—

	Carolina rice	Piedmont rice
Starch . . .	85·07	83·80
Woody fibre . .	4·80	4·80
Gluten . . .	3·60	3·60
Tallowy oil . .	0·13	0·25
Sugar, uncrystallisable	0·29	0·25
Gum	0·71	0·10

	The Ash
Potash	18·48
Soda	10·67
Lime	1·27
Magnesia	11·69
Oxide of iron	0·45
Phosphoric acid . . .	53·36
Chlorine	0·37
Silica	3·35

The following are by Blyth:—

Rice Grain	Per cent.
Water	14·41
Nitrogenous substance . .	6·94
Fat	0·51
Starch	77·61
Woody fibre	0·08
Ash	0·45

The Ash	Per cent.
Potash	21·73
Soda	5·50
Lime	3·24
Magnesia	11·20
Ferric oxide	1·23
Phosphoric acid . . .	53·68
Sulphuric acid	0·62
Silica	2·70
Chlorine	0·10

Kellner examined three kinds of Japanese rice with the following results:—

	Marsh Rice		Mountain Rice
	Ordinary	Glutinous	
Protein matter .	7·00	5·87	8·75
Fat . . .	2·29	3·44	2·58
Cellulose . .	4·58	5·19	1·98
Non-nitrogenous extract . .	84·76	83·89	85·53
Ash . . .	1·37	1·61	1·18

The figures for fat are higher than in other analyses of rice; but this is accounted for by the fact of the samples analysed being undressed grain, whereas other investigators have examined the dressed commercial article. For other analyses *v.* König, Chemie der menschl. Nahrungs- und Genussmittel.

RICINE *v.* VEGETO-ALKALOIDS.

RICINOLEIC ACID $C_{18}H_{34}O_3$. An acid occurring as a glyceride in castor-oil (*Ricinus communis*) and in the oil from the seeds of *Jatropha Curcas*. Best obtained by fractional precipitation of castor-oil soap by means of calcium chloride, the greater part of the calcium ricinoleate being contained in the last fractions (Claus and Hassenkamp, B. 9, 1,961). Is a thick, oily liquid, solidifying below 0°; soluble in alcohol and ether. By the action of nitrogen trioxide is converted into *ricinelaïdic acid*, a solid crystalline substance soluble in alcohol; m.p. 50°.

RICINUS OIL *v.* Castor oil; also Oils, fixed, and Fats.

RINMANN'S GREEN *v.* Cobalt.

RIONITE. A bismuth fahlore found at Cremenz, in the Canton Wallis.

ROBURITE *v.* Explosives.

ROCCELLA *v.* Archil (vol. i. p. 191) and Lichens (vol. ii. p. 464).

ROCCELLIC ACID $C_{15}H_{30}(CO_2H_2)$. An acid found in *Roccella fuciformis* and *Lecanora tartarea*. A white crystalline body; m.p. 130°; insoluble in water, readily soluble in alcohol and ether (Heeren, Schweig. Journ. 59, 346; Schunck, C. J. 3, 153; Hesse, A. 117, 332).

ROCCELLIN *v.* Azo- colouring matters.

ROCHELLE SALT *v.* Tartrates.

ROCK, ALUM. *Alunite v.* Alums (vol. i. p. 78).

ROCK CRYSTAL *v.* Quartz.

ROCK OIL *v.* Petroleum.

ROCK SALT *v.* Sodium chloride.

ROMAN ALUM *v.* Alums (vol. i. p. 78).

ROMAN CEMENT *v.* Cement (vol. i. p. 477).

ROMAN LAKE. *Crimson lake v.* Pigments.

ROMAN OCHRE. A variety of argillaceous ferric oxide of an orange-yellow colour, used as a pigment.

ROMITE *v.* Explosives.

ROSANILINE and **ROSANILINE DYES** *v.* Triphenyl methane colouring matters.

ROSCOELITE *v.* Vanadium.

ROSE BENGAL *v.* *Phthaleïns*, art. Triphenyl methane colouring matters.

ROSE OIL *v.* Oils, essential.

ROSE PINK. A pigment prepared by dyeing whiting with Brazil wood. It is too fugitive for artistic use, but is much employed in paper-staining.

ROSEÏNE. A synonym for fuchsine or aniline-red; *v.* Triphenyl methane colouring matters.

ROSENTHIEL'S GREEN or **CASSEL GREEN.** *Manganate of barium.* It is also known as manganese green. It is a very unstable pigment.

ROSEMARY OIL, *v.* Oils, essential.

ROSEWOOD, OIL OF. A volatile oil obtained from the wood of *Convolvulus scoparius* by distilling with water. A light-yellow oil consisting mainly of a terpene $C_{10}H_{16}$; b.p. 249°. Used occasionally for adulterating oil of roses.

ROSHYDRAZINE. The colour and leucobases of triphenylmethane, when diazotised and treated with $SnCl_2$, are readily converted into hydrazines. For example: Rosaniline (5 grms.) is dissolved in 30 c.c. of hydrochloric acid and 70 c.c. of water, and the iced solution is diazotised by adding 3½ grms. $NaNO_2$ in 10 c.c. of water. On mixing the solution of the diazo-compound with a well-cooled solution of 12 grms. of tin in 30 c.c. of hydrochloric acid, the *roshydrazine hydrochloride* separates out in green-shimmering crystals. The body is easily soluble in water, nearly insoluble in hydrochloric acid. Its solution has a bluer shade than rosaniline; it is a strong colouring matter, and dyes tannined cotton a deep brownish-red. Like other hydrazines, it reduces Fehling's solution, and forms condensation products with aldehydes and ketones. The latter compounds are sparingly soluble dyestuffs; thus acetone, aldehyde, pyruvic acid, benzophenone, &c., give reddish to bluish-violet colours; acetoacetic ether and benzaldehyde gave blues; whilst glucose gives a greyish-blue. Benzaldehyde sulphonic acid yields a blue soluble in water. These condensation-products can also be formed upon the fibre. The reduction of the diazo- compound of acid-magenta gives rise to easily-soluble sulphonic acids of roshydrazine, the condensation products of which are soluble colouring matters. Saffranine, when treated in the same way, does not give a hydrazine, but evolves nitrogen (J. H. Ziegler, B. 20, 1557–1558; S. C. I. 6, 594).

ROSINS *v.* Resins.

ROSIN OIL *v.* Resin oil.

ROSIN SPIRIT *v.* Resin oil.

ROSINDOLES *v.* Indoles.

ROSOCYANIN *v.* Turmeric.

ROSOLIC ACID *v.* Aurine.

ROSTHORNITE *v.* Resins.

ROTTENSTONE. A disintegrated rock which, when washed and ground, is used as a polishing material for metal, marble, &c. It is usually regarded as the residual matter left on the natural decomposition of impure limestone. If the limestone be siliceous, the silica may be left in a very finely-divided condition; but old analyses of Derbyshire rottenstone show a very large proportion of alumina. The rottenstone of Derbyshire occurs in irregular cavities in the carboniferous limestone, and the best kinds are said to be obtained from a black bituminous limestone near Ashford, and on Bakewell Moor. It has also been worked in South Wales, especially in the counties of Brecon, Carmarthen, and Glamorgan. The term 'rottenstone' is sometimes applied to *tripoli*, a material consisting of highly-comminated silica, which is mostly derived from the frustules or siliceous cases of the unicellular algæ known as diatoms. It is therefore similar to diatomaceous earth or kieselguhr (*q. v.*).

ROTTLERIN *v.* Resins.

ROUGE *v.* *Iron oxides*, art. Iron.

ROUILLE *v.* *Iron oxides*, art. Iron.

ROYAL BLUE. *Smalt v.* Cobalt; also Pigments.

RUBERYTHRIC ACID forms lemon-yellow silky needles melting at 258–260°. It is readily soluble in alcohol, and almost insoluble in ether and benzene. On boiling with either acids or alkalis it splits up into alizarin and grape sugar. It does not form lakes with mordants, nor does it ferment with yeast. Its Ba, Sr, and Ca salts form beautiful red precipitates from boiling aqueous solutions.

Schunck and Rochleder admitted the possibility that rubianic and ruberythric acids might be identical substances, and careful comparison of the two has proved the correctness of this theory. Liebermann and Bergami compared their glucoside with a sample of rubianic acid prepared by the late Dr. H. Römer in Dr. Schunck's laboratory. The results of the analysis of the free acids, and of their Ba and K salts, correspond better with the formula of Graebe and Liebermann—viz., $C_{26}H_{28}O_{14}$—than with that of Rochleder—viz., $C_{20}H_{22}O_{11}$. The latter formula is rendered more improbable, because according to his equation the decomposition of the glucoside into alizarin and sugar takes place under dehydration of the molecule:

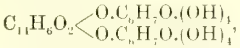
$$C_{20}H_{22}O_{11} = H_2O + C_{14}H_8O_4 + C_6H_{12}O_6;$$

whilst usually such decompositions are effected by hydration, which also is the case in the equation proposed by Graebe and Liebermann: $C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$. As further proof in favour of this equation, the ruberythric acid was dissolved in cold concentrated sulphuric acid; this solution, diluted with four times its weight of water, was then heated on a boiling-water bath for one hour, and after further dilution for other two hours, the amount of alizarin obtained was 43 p.c.; whilst the equation requires 42·5 p.c. However, the decomposition in like manner of the *octo-acetyl-ruberythric acid* $C_{26}H_{20}(OC_2H_3O)_8O_6$, and quantitative determination of the alizarin, grape sugar, and acetic acid formed, proved beyond doubt the identity of the two bodies, the reaction being as follows:

$$C_{26}H_{20}(OC_2H_3O)_8O_6 + 10H_2O$$
$$= C_{14}H_8O_4 + 2C_6H_{12}O_6 + 8C_2H_4O_2.$$

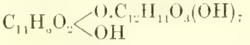
The above acetyl compound is readily formed by the usual method by means of acetic anhydride and acetate of soda. It forms bright-yellow needles soluble in cold glacial acetic acid, soluble with difficulty even in hot alcohol, and insoluble in water. It melts at 230°.

The constitution of ruberythric acid is usually expressed by the formula



$$C_{14}H_6O_2{<}\begin{matrix}O.C_6H_7O.(OH)_4\\O.C_6H_7O.(OH)_4\end{matrix},$$

in which both phenol-hydroxyl groups are combined with grape sugar, and which admits quite well of the formation of an octo-acetyl compound. However, the formula



$$C_{14}H_6O_2{<}\begin{matrix}O.C_{12}H_{11}O_3(OH)_7\\OH\end{matrix}$$

admits this equally well, and explains better why ruberythric is a strong *mono*-basic acid, decomposing carbonates and (even when heated) acetates of the alkalis. The fact that it does not form lakes with mordants, which might be urged in favour of the former formula, loses its significance, since it has been shown that substitution in only one hydroxyl group destroys the dyeing property of alizarin. However, it necessitates, what is not yet proved thoroughly, that the sugar combined with the alizarin should be a dextrose (C_{12} sugar group), which, on decomposition, must yield grape sugar (C. Liebermann and O. Bergami, B. 20, 2241–2247; S.C.I. 6, 722); *v.* GLUCOSIDES; also ALIZARIN AND ALLIED COLOURING MATTERS.

RUBIACIC ACID *v.* MADDER.

RUBIACIN *v.* MADDER.

RUBIADIN. *Rubianin v.* MADDER.

RUBIADIPIN *v.* MADDER.

RUBIAFIN *v.* MADDER.

RUBIANIC ACID *v.* RUBERYTHRIC ACID; also GLUCOSIDES, and ALIZARIN AND ALLIED COLOURING MATTERS.

RUBIDEHYDRAN *v.* MADDER.

RUBIDINE *v.* AZO- COLOURING MATTERS.

RUBIHYDRAN *v.* MADDER.

RUBIRETIN *v.* MADDER.

RUBRIC LAKE. *Madder lake v.* PIGMENTS.

RUBIDIUM. Rb. At. wt. 85·2 (Bunsen, Picard, Goddefroy). Rubidium was discovered by Bunsen and Kirchhoff by means of the spectroscope, immediately after the discovery of cæsium, in the Dürkheim water. It usually occurs with cæsium, being found in lepidolite and petalite, in many mineral springs, in the ashes of seaweed, tobacco, tea, &c., and of beetroot molasses; in crude cream of tartar, &c. (*v. also* CÆSIUM). Rubidium cannot replace potassium as a plant food.

It may be prepared by heating a mixture of sugar-charcoal, charred acid rubidium tartrate, and calcium carbonate at a white heat. It appears, like potassium, to form an explosive compound with carbon monoxide.

Rubidium is a silver-white, soft metal, melting at 38·5° (Bunsen), and evolving a bluish vapour at a dull-red heat. It oxidises rapidly in air, and decomposes water, with ignition of the liberated hydrogen.

With the exception of cæsium, rubidium is the most positive element. It forms one oxide; the hydroxide RbHO is very deliquescent, and dissolves in water and alcohol. Its salts correspond exactly with those of potassium, but impart a more reddish shade to the Bunsen flame than the salts of that metal.

RUBIN BUFFALO *v.* AZO- COLOURING MATTERS.

RUBRESSERINE *v.* ORDEAL BEAN.

RUBY *v.* CORUNDUM; also ALUMINIUM.

RUBY SULPHUR. *Realgar, Arsenic sulphide, v.* ARSENIC.

RUDDLE *v.* REDDLE.

RUE, OIL OF, *v.* OILS, ESSENTIAL.

RUFIGALLIC ACID or **RUFIGALLOL** $C_{14}H_8O_8$.

A body obtained by heating gallic or digallic acid with strong sulphuric acid. Is probably the anhydride of digallic acid (H. Schiff, B. 4, 967) or hexhydroxy-anthraquinone $C_{12}H_2(CO_2)_2(OH)_6$ (Jaffe, B. 3, 964).

RUFIMORIC ACID *v.* FUSTIC.

RUM is an ardent spirit, the product of distillation of saccharine matter. It is usually made from molasses, or from the skimmings of the sugar boilers and the waste of the crushing-house. The principal source of supply is the West India Islands and British Guiana, and the quality most esteemed is associated with the name of Jamaica. It is also distilled in France from beetroot.

The method of manufacture in Jamaica is by the use of a Pontifex still. To a given quantity of skimmings, molasses, and water, so proportioned that the saccharine matter contained in it may reach 12 to 16 p.c., an equal quantity of the lees of a previous distillation, called 'dunder' (Span. *redundar*, to be redundant), is added. Fermentation goes on for a period varying with the strength of the wort, careful testing being here necessary so as not to exceed the maximum of attenuation where acidulation supervenes. Being pumped into the still, the liquor is drawn over until no longer inflammable. After a second distillation of the low wines it is found that, approximately, 115 gallons of proof-spirit result from 1,200 gallons of wash containing originally about 12 p.c. of sugar; but this is by no means to be taken as a universal estimate, since the variation between the sugars of one district and those of another is considerable, and may give from 65 gallons per hogshead (16 cwt.) to 90 gallons per hogshead.

It is usually imported at a strength of 20° overproof; and the lowest limit of sale under the Food and Drugs Act, 1877, is 25° u.p.

Imports and Value.

Year	Imports	Value
	Proof gallons	£
1888	4,147,656	336,356
1889	4,120,358	342,978
1890	6,241,842	552,675

Rum-shrub is rum flavoured with orange lemon, and sugar.

RUST. The red or reddish-brown incrustation formed on iron and steel when exposed to ordinary atmospheric influences. Iron is not singular in this respect, as most other metals undergo some superficial change under similar circumstances. But with iron the change is rapid, and the film first formed, instead of protecting the metal beneath from further action, as is the case with other metals, continues to increase in thickness until a rough earthy crust is formed, which is easily detached in flakes. This process may continue until the iron is wholly converted into rust.

The change is finally one of oxidation, as rust consists mainly of partially-hydrated ferric oxide varying between Fe_2O_3 and $Fe_2(OH)_6$. But rust may contain notable quantities of ferrous iron, especially in the lowest layers next the metal. Rust is sometimes stated to contain ferrosoferric oxide Fe_3O_4; but this appears to be an assumption based merely on the coexistence in it of iron in the two states of oxidation. Rust may also contain additional substances derived from the elements admixed with the original iron, such as carbon, manganese, silicon, slag, &c.

The combined carbon of iron appears to be largely eliminated in the form of hydrocarbons during the rusting process, an occurrence which will subsequently be seen to be quite probable.

The graphitic carbon is unaffected, and in slow submarine rusting it is sometimes left as a spongy mass preserving the form of the original iron object.

The following are analyses of rust (Calvert):

—	Rust from Conway Bridge	Llangollen
Fe_2O_3 . . .	93·09	92·90
FeO . . .	5·81	6·12
$FeCO_3$ . . .	·90	·62
Silica . . .	·20	·12
Ammonia . .	traces	traces
$CaCO_3$ . . .	—	·29

The chemical changes causing the formation of rust were carefully studied by Crace-Calvert (C. N. 23, 98). Taking clean blades of metal, Calvert exposed them to different influences for four months, with the following results: I. In dry oxygen, no oxidation. II. In damp oxygen, only one blade in three slightly oxidised. III. In dry carbon dioxide, no oxidation. IV. In damp carbon dioxide, slight white precipitate of ferrous carbonate in four out of six blades. V. In dry carbon dioxide and oxygen, no oxidation. VI. In damp carbon dioxide and oxygen, oxidation most rapid, a few hours being sufficient; blade dark green, then brown ochre. As rust had been found to contain traces of ammonia, Calvert tried experimentally whether this substance accelerated rusting. He obtained a negative result. On the other hand, he found that rusting was prevented by the presence of alkalis or alkaline carbonates. He concluded from these experiments that carbonic acid played a leading part in ordinary aerial rusting.

It is well known that iron is attacked by an aqueous solution of carbon dioxide. The ferrous carbonate so formed dissolves in the excess of carbonated water; the iron in chalybeate water is usually as ferrous carbonate dissolved by a solution of carbonic acid. Chalybeate water exposed to the air soon becomes turbid, and forms an ochreous deposit consisting of ferric hydrate. These changes, which are identical with those that take place in rusting, may be expressed as follows:

$$Fe + H_2O + CO_2 = FeCO_3 + H_2$$
$$4FeCO_3 + 6H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2.$$

The carbon dioxide is thus eliminated at the end of the change, and may attack fresh portions of iron. The change, however, is by no means so rapid in its phases as many other chemical actions of a similar cyclical kind, for the lower layers of rust, as already stated, are often highly ferrous and greenish in colour. Ultimately they pass into the state of peroxidation. Rust is hygroscopic, and in this way tends to accelerate the rusting process. The elimination of combined carbon in the rusting process is explained by the action of the nascent hydrogen in the first stage of the change.

Though the chemistry of rusting may be expressed in a simple manner by the above equations, the actual change is complicated by several conditions of a physical kind. It must be remembered (1) that the material on which experiments have been made is not pure iron in the chemical sense, nor is it absolutely homogeneous; (2) that slight differences of composition or variations of structure may introduce a difference of electrical state; (3) that if these differences of electrical state are set up in iron, in contact with an oxidising medium like water, electrolytic action may ensue and greatly accelerate the oxidising action.

These considerations render it doubtful whether pure homogeneous iron would be any more subject to rust than, for example, is pure zinc to the action of sulphuric acid. They will also explain the fact that when iron is sealed up in air-free water, some action takes place, and a small amount of ferrous hydrate is formed. The effect of the difference of electrical state in the oxidation of metals may be easily shown by immersing pieces of iron and zinc in very dilute sulphuric acid. As soon as the ends projecting from the liquid are made to touch, the zinc dissolves rapidly; whilst hydrogen gas escapes briskly from the surface of the iron. The same thing may be shown by laying small bits of zinc and copper foil on the surface of a piece of iron which is kept wet. It is soon noticed that round the zinc, which is electro-positive to the iron, there is an area free from rust; whilst the copper, which is electro-negative to the iron, only serves to accelerate the formation of rust in its neighbourhood.

That comparatively small differences of composition are sufficient to cause such electrical effects, has been clearly shown by Andrews (Proc. Inst. C.E. 77, 332), who experimented with plates of iron and steel immersed in sea water.

It is also to be remembered that rust is electro-negative to iron, so that rust itself will accelerate rusting.

The above considerations will serve to explain the irregular action of rusting on one piece of metal. The fibrous structure of a piece of polished wrought-iron becomes apparent on rusting, owing to these local differences of chemical and physical character and the resulting galvanic effects.

The prejudicial effect, from a similar cause, of the layer of ferroso-ferric oxide on iron and steel plates is generally recognised, and it is a common practice to carefully remove this film by 'pickling' in acid or a solution of sal-ammoniac. It is on the same grounds desirable that in iron structures the bolts, rivets, &c., should be as nearly as possible of the same character as the main mass of metal.

The 'pitting' of iron and the formation of rust cones is usually attributed to a similar cause. The irregular distribution of manganese in the metal appears to be a fertile source of such local action, or the adhesion of specks of other metals may be an exciting cause. Pitting is especially liable to occur in iron which is submerged, as in ships' plates. This may, no doubt, be explained as above. In such a case the rust first forms a blister over the speck, and the action proceeds downwards.

The relative corrosibility of iron and steel is a matter concerning which accurate information is extremely desirable in view of the extended use of the latter for many purposes for which iron was formerly employed.

Elaborate experiments were made on the subject by Mallet, full details of which are to be found in the British Association Reports for 1838, 1840, and 1843. The interest of these experiments is, however, diminished by their having been undertaken before the modern steel processes had come into use.

The relative corrosibility of wrought-iron and steel has been much discussed in recent years, but unanimity of opinion does not prevail. It would appear difficult, however, to controvert the extremely careful experiments of Andrews (Proc. Inst. C.E. 77, 332, and ibid. 82, 281), who has investigated the simple and galvanic corrosion of various specimens of iron and steel when immersed in sea-water. The following tables, extracted from the paper just cited, set forth some of the chief results obtained by Andrews:—

Chemical analysis of the wrought-iron, steel, and cast-iron metal plates.

Description	Graphitic carbon	Combined carbon	Silicon	Sulphur	Phosphorus	Manganese	Iron (by difference)	Total
Wrought iron, No. 1	—	trace	0·206	0·024	0·454	0·396	98·920	100
,, No. 2 (Wortley best scrap)	—	none	0·392	0·034	0·270	0·194	99·110	100
Soft Bessemer steel	—	0·150	0·015	0·111	0·064	0·540	99·120	100
Soft Siemens-Martin steel	—	0·170	0·071	0·117	0·077	0·627	98·938	100
Soft cast steel	—	0·460	0·074	0·025	0·210	0·184	99·047	100
Hard Bessemer steel	—	0·510	0·068	0·113	0·087	1·153	98·069	100
Hard Siemens-Martin steel	—	0·720	0·080	0·102	0·143	1·239	97·716	100
Hard cast steel	—	1·407	0·121	0·056	0·080	0·360	97·976	100
Cast metal, No. 1	1·500	2·010	0·410	0·250	0·450	0·650	94·730	100
,, No. 2	2·620	0·670	1·940	0·090	0·950	0·520	93·210	100

Simple corrosion of plates.

Description	Combined carbon (see preceding table)	Loss per square foot of surface, after exposure singly in sea-water			
		After 4 weeks	After 56 weeks more	After 54 weeks more	During whole period of 114 weeks
		grains	grains	grains	grains
Wrought iron, No. 1	trace	34·40	114·68	169·70	318·78
,, No. 2 (Wortley best scrap)	none	—	97·99	139·27	—
Soft Bessemer steel	0·150	34·56	108·85	158·18	301·59
Soft Siemens-Martin steel	0·170	40·00	125·83	155·00	320·83
Soft cast steel	0·460	35·76	148·65	227·74	412·15
Hard Bessemer steel	0·510	38·96	134·92	199·68	373·56
Hard Siemens-Martin steel	0·720	34·24	122·14	173·24	329·62
Hard cast-steel	1·407	39·68	139·57	184·54	363·79
Cast metal, No. 1	2·010	—	160·62	254·25	—
,, No. 2	0·670	—	182·70	172·73	—

Plates of brightly-polished metal were immersed in wooden troughs filled with sea-water. In twenty-four hours wrought iron was covered with bubbles; on the Bessemer steel and soft cast steel there were none. In four days the bubbles disappeared, all the specimens corroding except the puddled steel. In seven days all the solutions were opalescent, yellow in colour, most markedly so in the case of soft cast steel, least so in wrought iron and puddled steel. After twenty-eight days the specimens were renewed, washed, cleaned free from rust, and re-immersed, being taken out and cleansed at intervals. Corrosion was found to go on at an increasing rate, being 50 p.c. more in the second than in the first year. As to soft steel plates, the lower the percentage of combined carbon the less the corrosion. The best scrap iron, No. 2, corroded, during 110 weeks, much less than the steel. Wrought iron, No. 1, containing roughly double the percentage of phosphorus and manganese, corrodes more than best scrap iron, but less than any of the steels, except the soft Bessemer steel. Manganese produced corrosion owing to its uneven distribution, thus causing local action.

With regard to the galvanic corrosion resulting from the contact of iron and steel, experiments were made to ascertain which of the two metals was electro-positive in the combination. It was found that the electrical state varied as the corrosion went on, sometimes one of the metals being electro-positive, sometimes the other.

Prevention of rust.—Owing to the rapidity with which rusting takes place, it is necessary that iron structures exposed to atmospheric influences, or immersed in water, should be subject to some protective treatment. The commonest method is to paint the structure. The composition of the paints varies very greatly, and it is impossible here to enter into details. It is important in applying the paint that the surface of the metal should be as clean and dry as possible, otherwise the film of paint may be broken and a weak spot be found at which rusting would occur. For treating certain objects, such as iron pipes, the process introduced by Angus Smith is largely used. In this process the tube or plate is heated to 700°F., and then dipped vertically into a mixture of coal-tar pitch, 5 or 6 p.c. of linseed oil, and sometimes a little rosin, heated to 300°F., allowed to remain in the mixture several minutes, withdrawn, and allowed to dry in a vertical position.

Another process in common use consists in galvanising the iron. In this process the surface of the iron is cleaned by dipping in dilute acid, the plate being afterwards dipped into molten zinc. The film of zinc formed serves as a protective superficial layer.

Enamelling may be used for small articles. The process introduced by Professor Barff, the modification of it by Mr. Bower, and the combination of the two, known as the Bower-Barff process, have been introduced within the last few years, and applied with success. In the Barff process, the iron to be protected was treated with superheated steam, whereby the surface was changed into magnetic oxide of iron. This substance is highly resistant to ordinary atmospheric influences. The writer has found that in the case of such hardly-used things as retort stands the protection is very efficient. In the Bower process, air at a high temperature is used for effecting the same change on the iron. In the Bower-Barff process the two agents are combined. A further modification of this process, recently introduced, is known as 'Gesner's process.' In this the iron is heated in ordinary gas retorts to a temperature of 1000 or 1200°F. for twenty minutes. Superheated steam is then passed in for thirty-five minutes, half a pint of naphtha is then added, and then superheated steam for fifteen minutes more.

Caustic alkalis and alkaline carbonates prevent the formation of rust. This fact may be put to practical use in the case of the interior of boilers. The corrosion of boilers may also be prevented by keeping them full of water when not in use, or by blowing off whilst hot (*v.* also Anticorrosive compositions and Methods, and Anti-fouling compositions, vol. i. p. 177). A. Sm.

RUSSET RUBIATE. *Rubens madder v.* Pigments.

RUTHENIUM *v.* Platinum metals.

RUTILE *v.* Titanium.

RUTIN *v.* Glucosides.

RYE *v.* Cereals.

S

SABADILLA *v.* *Veratrine*, art. Vegeto-alkaloids.

SACCHARIC ACID $C_6H_{10}O_8$ or
$CO.OH(CH.OH)_4COOH$.
An acid obtained by the oxidation of many carbohydrates; more particularly those which yield dextrose on hydrolysis. Best prepared by the action of nitric acid on starch (Sohst and Tollens A. 245, 1). Has no action on Fehling's solution, but reduces ammoniacal solutions of gold and silver. By continued action of nitric acid yields tartaric and racemic acids, and ultimately oxalic acid. On distillation it yields *pyromucic* and *isopyromucic acids*, with evolution of carbon dioxide. Forms well-defined normal and acid salts with the alkalis, the former readily and the latter sparingly soluble in water.

SACCHARIMETRY *v.* Sugar.

SACCHARIN $C_6H_{10}O_5$. A white crystalline substance forming large rhombic prisms of a bitter taste obtained by gently heating solution of invert sugar dextrose or lævulose with lime (for details *v.* Kiliani, B. 15, 2954). The solution is filtered, the excess of the lime is removed by carbonic acid, and the clear concentrated liquid allowed to stand. M.p. 161–162°. Soluble in 7·7 parts of cold water; specific rotation +93·5.

Iso-saccharin, a substance obtained by Cuisinier by the action of lime on maltose and milk-sugar. (For details of preparation *v.* Kiliani, B. 18, 631.) Forms large crystals much more soluble in water than saccharin. M.p. 95°. Dextrorotatory.

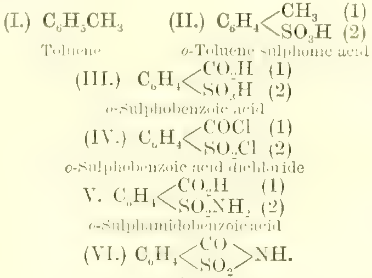
Meta-saccharin, also obtained by the action of lime on milk-sugar. M.p. 141–142°. Rotates the plane of polarisation to the left.

SACCHARINE. *Anhydro-sulphamido-benzoic acid.* This substance was discovered by Fahlberg in 1879 (B. 12, 469), and is the anhydro-compound of ortho-sulphamido-benzoic acid. It is produced commercially by heating toluene with ordinary concentrated sulphuric acid (66° Bé.) at a temperature below 100°. Ortho- and para-toluene sulphonic acids are formed, the first-named under these conditions being present to the extent of about 40–50 p.c. The mixture of acids is then treated in one or two different ways. The method now adopted will be described last.

The mixture of sulphonic acids is converted into the sodium salt, which is then treated with phosphorus pentachloride. On a large scale this is modified by mixing the sodium salt with phosphorus trichloride, and passing chlorine through the mixture. For the preparation of large quantities of phosphorus trichloride Fahlberg has devised new apparatus in which yellow phosphorus is used, and a continuous supply allowed to pass into the apparatus by means of a funnel. The mixture of trichloride and sodium salt is heated during the time chlorine is passed through to a temperature below boiling-point of the former, and at the end of the reaction the phosphorus oxychloride produced is distilled off. On cooling the mixture of *o*- and *p*-toluene sulphochlorides, the latter crystallises out. The *o*-toluene sulphochloride is acted on with dry ammonia, or, better, is heated with ammonium carbonate or bicarbonate. The *o*-toluene sulphamide found is scarcely soluble in water, and is thus separated from the ammonium chloride produced. It is then oxidised in a dilute neutral solution with potassium permanganate. Dilute acid must be added from time to time to keep the solution neutral. A solution of the potassium salt of benzoësulphaminic acid—*i.e.* *o*-sulphamido-benzoic acid—together with manganese hydroxide is formed, and on filtration from the latter saccharine is precipitated by means of an acid. The *p*-toluene sulphochloride is mixed with charcoal and heated in autoclaves under pressure with superheated steam, yielding toluene, hydrochloric, and sulphuric acids. The phosphorus oxychloride produced is used in the preparation of chlorine by heating it with bleaching powder and water.

The present method, however, differs somewhat from the above, and is said to give a better yield. The mixture of the *o*- and the *p*-toluene sulphonic acids is subjected to oxidation, with the formation of about equal quantities of *o*- and *p*-sulpho-benzoic acids. These are converted into the potassium salts, and after having been carefully dried are converted into the dichlorides by means of the action of chlorine in presence of phosphorus trichloride. The two dichlorides show a different behaviour towards ammonia. That of the para- derivative is converted into a diamide which is only slightly soluble in water, whereas the ortho- derivative yields the ammonium salt of *o*-sulphamidobenzoic acid, which is very easily soluble in water. Hence after the chlorination is completed, the phosphorus oxychloride is distilled off and the calculated amount of ammonium carbonate is added. The reaction is commenced by gentle heating, and is completed preferably in an atmosphere of carbonic acid. The insoluble *p*-diamide is filtered off, and the filtrate, on decomposing with an acid, yields saccharine.

The successive operations can be represented as follows:



(I.) $C_6H_5CH_3$ Toluene

(II.) $C_6H_4<\begin{matrix}CH_3 & (1)\\ SO_3H & (2)\end{matrix}$ *o*-Toluene sulphonic acid

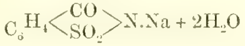
(III.) $C_6H_4<\begin{matrix}CO_2H & (1)\\ SO_3H & (2)\end{matrix}$ *o*-Sulphobenzoic acid

(IV.) $C_6H_4<\begin{matrix}COCl & (1)\\ SO_2Cl & (2)\end{matrix}$ *o*-Sulphobenzoic acid dichloride

V. $C_6H_4<\begin{matrix}CO_2H & (1)\\ SO_2NH_2 & (2)\end{matrix}$ *o*-Sulphamidobenzoic acid

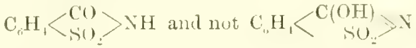
(VI.) $C_6H_4<\begin{matrix}CO\\ SO_2\end{matrix}>NH.$ Saccharine

Saccharine is a white crystalline solid possessing an intensely sweet taste, and is said to be 280 times sweeter than cane-sugar. It melts at 224°, and is sparingly soluble in water but more so in alcohol. On neutralisation with sodic hydrate or carbonate the sodium salt of saccharine which crystallises in large rhombic plates is obtained. Its constitution is



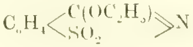
$$C_6H_4<\begin{matrix}CO\\ SO_2\end{matrix}>N.Na + 2H_2O$$

It loses its water of crystallisation at 80°, more quickly when heated to 150°. Like saccharine, it has an intensely sweet taste. On heating the dry salt with ethyl iodide in sealed tubes to 230 the ethyl ether of saccharine is obtained, sodium iodide separating out. The ether melts at 94°, is more soluble in hot than in cold water, and is very easily soluble in alcohol and ether. Unlike saccharine and its salts, it is absolutely tasteless. Saccharine, on heating with hydrochloric acid, decomposes into *o*-sulphobenzoic acid and ammonia, or rather ammonium chloride. Similarly, the ether splits up into *o*-sulphobenzoic acid and ethylamine, according to the following equation: $C_9H_9SO_3N + 2H_2O = C_7H_6SO_5 + C_2H_7N$. This decomposition proves that the constitutional formula of saccharine is



$$C_6H_4<\begin{matrix}CO\\ SO_2\end{matrix}>NH \text{ and not } C_6H_4<\begin{matrix}C(OH)\\ SO_2\end{matrix}>N$$

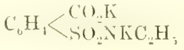
since an ether having the composition



$$C_6H_4<\begin{matrix}C(OC_2H_5)\\ SO_2\end{matrix}>N$$

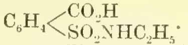
would have yielded alcohol and *o*-sulphobenzoic acid.

The ethyl ether of saccharine is not acted on by aqueous potash, but alcoholic potash forms the dipotassium salt of *o*-ethylamidosulphobenzoic acid, having the composition



$$C_6H_4<\begin{matrix}CO_2K\\ SO_2NKC_2H_5\end{matrix}$$

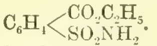
and this on decomposition yields *o*-ethylamido-sulphobenzoic acid



$$C_6H_4<^{CO_2H}_{SO_2NHC_2H_5}.$$

This substance crystallises in needles, is tolerably soluble in water, and very soluble in alcohol and ether. It has no sharply defined melting-point, but commences to fuse at 102°, and is completely liquid at 116°.

The isomeric compound—*i.e.* the ethyl ether of *o*-sulphamido-benzoic acid—is obtained by passing hydrochloric acid through absolute alcohol containing saccharine, or by heating *o*-sulphamido-benzoic acid with ethyl iodide and sodium ethylate with an inverted condenser. Its constitution is



$$C_6H_4<^{CO_2C_2H_5}_{SO_2NH_2}.$$

It melts at 83°, is slightly soluble in cold and very soluble in boiling water, alcohol, and ether, and crystallises in long white needles. If simply suspended in water and the equivalent amount of sodium hydrate is added, the solution reacts neutral and tastes sweet; in fact, saccharine is formed, which may be precipitated by adding an acid. Acids also decompose the ether, and even on boiling with water it is slowly converted into alcohol and saccharine (Fahlberg and List, B. 20, 1603; *cf.* Witting, Chem. Zeit. 11, 314).

Detection.—The tests for Fahlberg's saccharine (orthosulphamine-benzoic acid) depending on the formation of ammonia or the alkaline sulphides, are scarcely of sufficient delicacy or convenience for the detection of minute quantities—as, for instance, in wine. The following, based on the formation of salicylic acid during the fusion of saccharine with alkalis, is recommended where salicylic acid is not already present in quantities sufficient to impair the delicacy of the reaction. The wine is rendered strongly acid, and 100 c.c. are shaken three times successively with 50 c.c. of a mixture of equal volumes of ether and light petroleum. The united extracts are evaporated after the addition of some caustic soda, and the residue is heated at 250° for half-an-hour with 0·5 or 1 grm. of solid caustic soda. The fused mass is dissolved in water, and the salicylic acid separated and detected in the usual manner. In this manner 0·005 p.c. of saccharine, or even less, may be detected. The mixture of equal volumes of ether and light petroleum, an excellent solvent for saccharine, does not dissolve tannin and such like substances, which also form salicylic acid when fused with alkalis, and would interfere with the test if they were extracted. Potash cannot be used for the fusion in place of soda (C. Schmitt, Rep. Anal. Chem. 7, 437–441; S. C. I. [6], 681).

If the substance is dissolved in strong (25–30 p.c.) caustic potash solution, and bromine added drop by drop until a permanent yellow colouration is obtained, a yellow pasty precipitate separates after a certain time, depending upon the concentration of the solution. This precipitate is crystalline. Heated on platinum foil it froths up, without melting, in a vermicular form and burns, leaving a voluminous residue containing potash. If water is added and heated, bromine is evolved and the residue dissolves slowly. On cooling, yellow crystals separate, having pointed ends. Another property of saccharine is the formation of a substance similar to fluorescein on heating with resorcinol. The saccharine is heated with a slight excess of resorcinol, and a few drops of concentrated H_2SO_4 until it begins to swell up. The flame is then removed until the reaction slackens, when the heating is repeated. On diluting with water and adding potash, a strongly green fluorescent solution is obtained. The saccharine is extracted from the substance to be analysed with ether after acidifying with sulphuric or phosphoric acid (supposing the saccharine to be present as potassium salt in solution) and the ether distilled off (E. Börnstein, Fr. 27, 165–168; S. C. I. [7] 458).

If saccharine be evaporated with nitric acid on the water-bath, the residue allowed to cool, and a few drops of a strong solution of potash in 50 p.c. alcohol added, a faint yellow colour is developed; on spreading the liquid over the surface of the dish, and then applying heat rapidly, streaks of blue, violet, and red are developed (S. C. I. 1888, 772).

SACCHARINIC ACID $C_6H_{12}O_6$. An unstable acid obtained as the calcium salt by boiling solutions of saccharin with freshly precipitated chalk (Scheibler, B. 13, 2212; Kiliani, A. 218, 373; Liebermann and Scheibler, B. 16, 1821; Hermann and Tollens, B. 17, 1333). *Iso-* and *meta-saccharinic acids* are formed as calcium salts by the action of lime on milk-sugar.

SACCHARONE $C_6H_8O_6.H_2O$. A body obtained by the action of nitric acid on saccharin.

SACCHAROSES *v.* Sugar.

SACRED BARK *v.* Cascara sagrada.

SAFFLOWER (*bastard saffron*). This dyestuff consists of the dried florets of *Carthamus tinctorius*, an annual thistle-like plant belonging to the *Cynarocephalæ*. A native of Southern Asia, it has been cultivated in China, India, Persia, Egypt, also in central and southern Europe. When in full bloom the yellow florets are plucked, and either at once dried, so as to form an orange-coloured fibrous mass somewhat resembling saffron, or they are first kneaded with water, in order to remove a useless yellow colouring matter, and then pressed into the form of lens-shaped cakes and dried.

Safflower owes its value to an insoluble red colouring matter which occurs only in very small amount, about 0·5 p.c., whereas the soluble yellow colouring matter is present to the extent of about 30 p.c.

The yellow colouring matter may be obtained by first precipitating an aqueous extract of safflower with lead acetate and acetic acid, and then adding ammonia to the filtrate, *i.e.* precipitating with basic lead acetate. The yellow precipitate thus obtained is carefully decomposed with dilute sulphuric acid, and after removing the lead sulphate the filtrate is evaporated to dryness with exclusion of air. It is thus obtained as an amorphous substance, having acid properties, a bitter taste, and a peculiar odour. It is of a very unstable character, and on exposure to air seems to oxidise, becoming brown and somewhat insoluble in water. According to Schlieper, its composition is represented by the formula $C_{16}H_{20}O_{10}$; according to Malin, it is $C_{24}H_{30}O_{15}$.

Carthamin or *carthamic acid* is the name given to the useful red colouring matter, which, though insoluble in water, is readily soluble in alkaline solutions. To obtain it, safflower is well washed with slightly acidulated water to remove the yellow colouring matter, then it is steeped for some time in a cold dilute solution of sodium carbonate. If to the alkaline solution thus obtained an acid were added, the carthamin would be precipitated, along with certain impurities which it would be difficult afterwards to remove. Their separation is, however, effected in a simple manner by making use of the fact that carthamin is readily attracted and removed from its acidulated solution by cellulose, whereas the impurities are left behind. Hence bleached cotton is immersed and moved about in the alkaline solution, which is at the same time gradually acidified with tartaric or citric acid.

In this manner the carthamin is slowly precipitated and at once attracted by the cotton, which thus becomes dyed red. After washing the dyed cotton with slightly acidulated water, the colouring matter is dissolved off by means of a dilute solution of sodium carbonate, from which the carthamin is thrown down, on the addition of tartaric acid, as a bright-red precipitate. Further purification is effected by dissolving the dried precipitate in alcohol and reprecipitating with water.

Carthamin is a bright-red amorphous powder insoluble in ether, very sparingly soluble in water, but soluble in alcohol. In a dry compressed condition it exhibits a yellowish-green metallic lustre. Boiled with water or alcohol, or on long exposure to air, it undergoes decomposition. In alkalis it dissolves with the formation of yellow-coloured alkaline carthamates, from the solutions of which it is precipitated by acids. By fusion with caustic potash it yields oxalic acid and para-oxybenzoic acid. With concentrated sulphuric acid it gives a red solution not precipitated by addition of water. An alkaline solution of carthamin added to metallic salt solutions gives orange-, yellow-, or brown-coloured lakes.

Carthamin is now sold in a more or less pure condition as a thin aqueous paste in stoneware bottles, under the name of *Safflower extract* or *Safflower carmine.*

The formula of carthamin is given variously as $C_{14}H_{16}O_{14}$ (Schlieper) and $C_{16}H_{17}O_7$ (Dumas, A. 27, 147).

Previous to the discovery of the coal-tar eosins safflower was frequently used for the production of brilliant pinks or reds, chiefly on cotton and silk. Even now it is still occasionally employed by the dyer of cotton or flax thread, tape, string, &c., notwithstanding the extremely fugitive character of the colour towards light, because of its brilliancy and the facility of its application.

The mode of dyeing is practically the same as that already given in describing the process of obtaining carthamin. The safflower, inclosed in bags, is well washed with cold water, preferably slightly acidulated, in order to remove the yellow colouring matter, and the red colouring matter is then extracted by a treatment with a cold dilute solution of sodium carbonate. In this solution the material to be dyed is worked about, at the same time adding 'lime juice' (citric acid) gradually till in slight excess. Safflower-extract is applied in a similar manner.

Dyers usually give the washed safflower several successive treatments with alkali, employing at first weak and afterwards strong alkaline solutions. The weak solutions give the brightest and purest tints; hence very delicate colours are dyed with these alone, while full colours are first dyed with the inferior extracts, and then 'topped' or 'bloomed' by dyeing in the purer solutions.

Carthamin ground up with starch, talc, &c., is used as rouge.

Literature.—Dumas, A. 27, 147; Liebermann, B. 7, 247; 8, 1,649; Döbereiner, Journ. Ch. Phys. 26, 266; Schlieper, A. 58, 357; Salvetat, Ann. Ch. Phys. [3] 25, 337; J. pr. 44, 475; Malin, Sitz. W., June 29, 1865; Dufour, A. Ch. 48, 283. J. J. H.

SAFFRANINES *v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM.

SAFFRANISOL *v.* AZINES.

SAFFRON BRONZE *v.* TUNGSTEN.

SAFFRON SURROGATE *v.* VICTORIA YELLOW.

SAFFRON YELLOW *v.* NAPHTHALENE.

SAFROSINE *v.* *Phthaleïns*, art. TRIPHENYLMETHANE COLOURING MATTERS.

SAGAPERUM *v.* GUM RESINS.

SAGE CAMPHOR *v.* CAMPHORS.

SAGE OIL *v.* OILS, ESSENTIAL.

SAGO. A granulated or powdered form of starch obtained from the pith of the trunk of *Sagus lævis* and *S. Rumphii* in Singapore, the former variety furnishing most of the sago sent to Europe. In India it is obtained from *Phœnix farinifera*; and in Java from *Corypha gebanga*; it is also produced by *Caryota urens* and several other palms and *Cycadaceæ.*

The pith, being removed from the bark which contains it, is reduced to powder; and after being mixed with water is strained through sieves, the starch falling through with the liquor and the cellular tissue being retained. The farina thus carried through the sieve and deposited in pans is further washed and dried, when it is fit for exportation.

Under the microscope, sago starch exhibits granules of elongated form and considerable size; one end of the granules being larger and rounded, the other smaller and truncate.

Granulated sago is a preparation from sago meal made by mixing the meal with water and passing the mixture through a sieve, the granules being caught in a heated vessel, so that they are slightly baked. By this process the starch cells are made to assume a much larger and less regular form than that of raw sago, effects which are due to the heat employed.

Portland sago is a kind of arrowroot, manufactured from the cormus of *Arum maculatum* in the island of Portland.

SAINT IGNATIUS'S BEAN *v.* NUX VOMICA.

SAKE. A very popular drink in Japan. It is prepared from rice by fermentation, the manufacture being carried on from September to February only, as in the summer the fermentation cannot be properly controlled. It is a pleasant, light-yellow liquid, smelling of alcohol, its specific gravity is about 0·99, and it contains on an average 15 p.c. of alcohol.

The manufacture takes place in three stages:

1. *Preparation of koji.*—The finest rice is boiled in an iron kettle with sufficient water to soften it; after cooling, it is brought into the koji chamber, the outside walls of which are covered with earth and the interior with straw, by which means the temperature of the interior is kept up.

The rice is here mixed with a little *moyaschi* (a yeast obtained from a previous fermentation) and remains in the chamber for two days, by which time most of the starch of the rice is converted into dextrose, and it is then called *koji*.

2. *Preparation of motoh.* — *Koji*, fresh-boiled rice, and water are mixed in a wooden vat in the proportion to form a thin paste. Wooden casks containing warm water are placed in this liquid every day; after one or two days a frothy fermentation takes place, which is allowed to continue 30–40 days, during which time the temperature rises to 37°C.; at the end of the period the liquid contains 10 p.c. of alcohol, and is called *motoh*.

3. *The third stage.*—Freshly boiled rice, *koji*, and *motoh* are mixed with a little water. The mixture ferments a little, but without appreciable rise in temperature. As soon as the froth ceases to form on the surface, *i.e.* in 8–10 days, the process is finished. The fermented fluid is filtered through cotton bags and put into casks, and allowed to stand till clear. It is heated in an iron vessel to 44°C., and is then run into casks.

The residue remaining in the cotton sacks has been used from time immemorial in Japan for the manufacture of vinegar (M. Ikuta, Z. 14, 439; S. C. I. 9, 754).

SAL ACETOSELLÆ. *Acid potassium oxalate* v. Oxalic acid.

SALAERATUS. A term applied in the United States to a baking powder consisting of a mixture of carbonate of soda, salt, and cream of tartar or tartaric acid.

SAL ALKALI MINERALE. *Sodium carbonate.*

SAL ALKALI VEGETABILE. *Potassium carbonate.*

SAL ALKALI VOLATILE SICCUM or **SAL VOLATILE.** *Ammonium sesquicarbonate.*

SAL AMARUM. *Magnesium sulphate.*

SAL AMMONIAC. *Ammonium chloride.*

SAL APERITIVUM FRIEDERICIANUM. *Sodium sulphate.*

SAL AURI PHILOSOPHICUM. *Acid potassium sulphate.*

SAL CATHARTICUM. *Magnesium sulphate.*

SAL CORNU CERVI. *Ammonium carbonate.*

SAL DE DUOBUS or **SAL DUPLICATUM.** *Normal potassium sulphate.*

SAL DIGESTIVUM SYLVII or **SAL FEBRIFUGUM SYLVII.** *Potassium chloride.*

SAL FUSIBILE. *Sodium ammonium phosphate.*

SAL MARINE. Common salt or *Sodium chloride.*

SAL MARTIS. Green vitriol or *Ferrous sulphate.*

SAL MICROCOSMICUM. *Sodium ammonium phosphate.*

SAL MIRABILE. *Sodium sulphate.*

SAL MIRABILE PERLATUM. *Disodium orthophosphate.*

SAL NARCOTICUM VITRIOLI. *Boric acid.*

SAL NATIVUM. *Sodium ammonium phosphate.*

SAL POLYCHRESTUM GLASERI, S. LAMERIANUM, S. PARISIENSE. *Normal potassium sulphate.*

SAL POLYCHRESTUM SEIGNETTI. *Rochelle salt*; *Sodium potassium tartrate.*

SAL PRUNELLA. Fused nitre cast into sticks or balls.

SAL SATURNI. *Lead acetate.*

SAL SECRETUM GLAUBERI. *Ammonium sulphate.*

SAL SEDATIVUM HOMBERGII. *Boric acid.*

SAL SUCCINI. *Amber.*

SAL TARTARI. *Potassium carbonate.*

SALENIXON. Crude potassium sulphate, as obtained in the manufacture of nitric acid.

SALEP GUM v. Gums.

SALICIN v. Glucosides.

SALICYLALDEHYDE $C_6H_4(OH)CHO$ (1, 2). Occurs in the oil from *Spiræa ulmaria* and other species of *Spiræa*. Obtained, along with the isomeric parahydroxybenzaldehyde, by the action of chloroform on an alkaline solution of phenol (Tiemann and Reimer, B. 9, 824; Tiemann and Herzfeld, B. 10, 63 and 213):

$$C_6H_5.OH + CHCl_3 + 4NaOH$$
$$= C_6H_4(ONa)CHO + 3NaCl + 3H_2O.$$

One part by weight of phenol, with 2 parts of caustic soda, is dissolved in at least 4 parts of water; the solution is heated to 50–60° in a flask fitted with a reflux condenser, and 2 parts of chloroform are gradually added, shaking continually. The colour of the liquid changes from yellow to deep red. The reaction is completed by boiling the mixture for half an hour, after which the excess of chloroform is distilled off. The liquid is then acidified with sulphuric acid and steam-distilled, when salicylaldehyde passes over, along with unchanged phenol. The liquid remaining in the retort is filtered hot; on cooling, it deposits crystals of parahydroxybenzaldehyde. The salicylaldehyde is separated from the phenol by shaking an ethereal solution of the two substances with hydrogen sodium sulphite, with which the salicylaldehyde forms a crystalline compound; this is separated, and decomposed by treatment with sodium carbonate or dilute sulphuric acid, when the aldehyde is liberated.

Salicylaldehyde is also formed when salicin $C_{13}H_{18}O_7$ is oxidised with a mixture of potassium bichromate and dilute sulphuric acid (Schiff, A. 150, 193).

Liquid, with a pleasant aromatic odour. Solidifies at −20° in large crystals, and boils at 196·5°. Sp.gr. 1·1731 at 13·5°. Somewhat soluble in water, miscible in all proportions with alcohol and ether; the aqueous solution gives a strong violet colouration with ferric chloride. By reduction it yields saligenin $C_6H_4(OH)CH_2OH$; on oxidation, salicylic acid. When boiled with acetic anhydride and anhydrous sodium acetate it forms coumarin (*q. v.*). Forms salts with bases: thus $C_6H_4(OK)CHO$ and $C_6H_4(ONa)CHO$; the alkali salts are not decomposed by carbon dioxide. By warming together salicylaldehyde, phenol, glacial acetic acid, and concentrated sulphuric acid, Liebermann (B. 9, 801; 11, 1436) obtained *hydroxy-aurin* $C_{19}H_{14}O_4$, a violet-red colouring matter. Zulkowsky found, among the products of the same reaction, an orange colouring matter which he termed *aurone*, assigning to it the formula $C_{26}H_{20}O_6$.

The isomeric *parahydroxybenzaldehyde* $C_6H_4(OH)CHO$ (1, 4), obtained as described in the foregoing, crystallises from water in needles melting at 115–116°. The solution gives a very faint violet tinge with ferric chloride.

F. R. J.

SALICYLIC ACID *v.* Hydroxy- acids.

Detection of salicylic acid in beer.—To 50 c.c. of beer in a separation funnel are added 5 c.c. of alcohol (to promote separation of the extracting liquid), 5 c.c. of sulphuric acid (1 in 10), and 50 c.c. of a mixture of equal volumes of ether and petroleum spirit, and the whole is thoroughly shaken. The ethereal extract is distilled to a small bulk, and the residue is shaken up with a few centimetres of water and a few drops of a weak ferric chloride solution. In presence of salicylic acid, the aqueous layer assumes a splendid violet colouration (J. Pinette, Chem. Zeit. 14, 1570–1571; S. C. I. 10, 165.

SALICYLIC YELLOW, SALICYLIC ORANGE. The preparation of these colouring matters from sulphosalicylic acid by nitration and bromination has been patented by the Chemische Fabrik auf Actien. (vorm. E. Schering) (Germ. Pat. 15,117, Dec. 10, 1880; 15,889, March 18, 1881; both expired April 1883). The former is said to dye wool and silk yellow, the latter dark golden yellow or orange.

SALOL. A combination of about 60 p.c. of salicylic acid and 40 p.c. of phenol, first introduced by Von Nencki, of Berne, as an antipyretic, and patented in Germany and the United States. It is a white crystalline powder, having the smell and taste of winter-green. Insoluble in water and dilute acids, but soluble in alcohol and alkalis. Melts at 45°. Appears to be excreted as urate of salicyl and sulpho-phenol. Used in medicine as a substitute for sodium salicylate (*v.* J. Moss, Year-Book of Pharmacy, 1886, 526). The alcoholic solution is coloured red-brown by ferric chloride. According to Sahli, it acts at least as powerfully as sodium salicylate, and it is also recommended as an antipyretic and antiseptic (E. Ghillany, Zeit. Oesterr. Apoth. Ver. 24,229; S. C. I. 5, 501). *V.* Disinfectants; also Hydroxy- acids.

SALSEPARIN *v.* Sarsaparilla.

SALT, COMMON, *v. Sodium chloride*, art. Sodium.

SALT, EPSOM. *Crystallised magnesium sulphate.*

SALT, FUSIBLE. *Sodium ammonium phosphate.*

SALT, GLAUBER'S. *Sodium sulphate.*

SALT, GLAZIER'S. *Potassium sulphate.*

SALT, MICROCOSMIC. *Sodium ammonium phosphate.*

SALT OF AMBER. *Succinic acid.*

SALT OF LEMERY. *Potassium sulphate.*

SALT OF LEMONS *v.* Oxalic acid.

SALT OF SATURN. *Lead acetate.*

SALT OF SODA. *Sodium carbonate.*

SALT OF SORREL *v.* Oxalic acid.

SALT OF TARTAR. *Potassium carbonate.*

SALT OF TIN. *Stannous chloride.*

SALT OF VITRIOL. *Zinc sulphate.*

SALT PERLATE. *Sodium phosphate.*

SALTPETRE. *Nitre; potassium nitrate.*

SALT SEDATIVE. *Boric acid.*

SALVIOL *v.* Camphors.

SALZBURG VITRIOL *v.* Copper sulphate.

SAMARIUM *v.* Cerium metals.

SAMARSKITE *v.* Cerium metals.

SAND. (*Sable*, Fr.) An accumulation of grains of mineral matter resulting from the disintegration of rocks. It is generally siliceous, since quartz is the most abundant rock-constituent, and by its hardness survives after the associated minerals have disappeared. The microscopic studies of Sorby, Phillips, and others have shown that in some sands a growth of crystalline quartz surrounds the original water-worn grains, the secondary deposit and the nucleus being in optical continuity (Quart. Journ. Geol. Soc. 36, 1880, 46; 37, 1881, 21). In sands derived from granitic rocks and crystalline schists, the quartz is often associated with grains of felspar and scales of mica; and A. Dick has pointed out the occurrence in such sands of zircon, rutile, and tourmaline (Nat. 36, 1887, 61). Many sands are coloured yellow or brown by ferric hydrate, while others are speckled with dark-green grains of glauconite. 'Black sand' usually contains magnetite, ilmenite, or cassiterite; the titaniferous iron-sand of Taranaki, in New Zealand, and that of the coast of Labrador, have been used as ores. 'Gem sands' vary in nature according to the character of the rocks which yielded them, but frequently contain garnets, spinels, and zircons. 'Volcanic sand' is composed of finely-divided lava.

Most sands have been deposited as sediments in water, either fresh or salt; but there are also accumulations of wind-drifted materials, known as *Æolian sands*, occurring as dunes along the coast or in the interior of deserts. The grains of desert sand are usually much more rounded than those of water-borne sand. Blown sand exerts considerable abrasive power, wearing any isolated rocks into characteristic forms: the *débris* caught by the wind scours the surface, but, not rising high, its action is mainly directed to undercutting the rock, thus tending to produce a tapering base and mushroom-like shape (J. Walther, Die Denudation in der Wüste, Leipzig, 1891). The eroding action of blown sand is taken advantage of in the *sand blast*, introduced by Mr. Tilghman. By this process, glass and stone may be rapidly engraved or cut by the action of a jet of sand projected with great velocity by means of steam or compressed air.

Siliceous sand, as free as possible from iron, is valued in the manufacture of glass. Good glass-making sand is dug at Alum Bay, in the Isle of Wight; at Lynn, in Norfolk; and near Reigate, in Surrey; and is largely imported from Fontainebleau, in France. Excellent sand occurs at Gweedore, in county Donegal. Sand is also used in the preparation of mortar, for which purpose it should be sharp and clean.

Sand is largely used as a moulding material for foundry work. The best moulding sand is argillaceous, containing in some cases as much as 6 p.c. of clay. Where a strong adhesive material is required, as for cores in casting, a clayey sand is especially needful. The foundry sand, or loam, is usually prepared by sifting, and may often be advantageously mixed with coke dust. Facing sand should be coated with carbonaceous matter, such as powdered charcoal or graphite.

It is a curious fact that many sands emit a musical sound when in motion. Jebel Nagous, or 'Mountain of the Bell,' on the Gulf of Suez, is so named in consequence of its acoustic phenomena. The sonorous sand of Eigg has long been known. Musical sand has been found in Studland Bay and elsewhere by Mr. Carus-Wilson. He regards the sound as due to the friction of innumerable grains of perfectly clean sand, free from angularity and of uniform size; and he has produced notes from sand otherwise non-musical (C. N. 64, 1891, 25; Nat. 44, 322). H. Carrington Bolton and A. A. Julien have studied the sonorous sands of various parts of America, and the 'barking sands' of the Sandwich Islands; the latter are calcareous sands (Proc. Am. Ass. Adv. Sc. 38, 1889). The grains of such sands are much rounded, and are exceptionally free from solid adherent matter; but it appears essential that they should be separated by a film of vapour. If the vapour, or cushion of air between the grains, be removed by heating, rubbing, or shaking them, the sand becomes mute.

Fulgurites, or 'lightning tubes,' are occasionally formed when lightning strikes a sandy soil, the walls of the tubes becoming vitrified by the heat. F. W. R.

SANDAL, SANDEL, or **SANTAL WOOD** *v.* Sanderswood.

SANDALWOOD CAMPHOR *v.* Camphors.

SANDARAC *v.* Resins.

SANDARACIN *v.* Resins.

SANDERSWOOD (*Red Saunderswood*, *Santalwood*, *Sandelwood*). This dyestuff is classed along with *Barwood*, *Camwood*, and *Caliatour* or *Cariatour-wood*, since they all possess very similar dyeing properties, and, owing to the insolubility in water of the resinous colouring matters they contain, they are called the *insoluble red woods.* They cannot, therefore, be made to yield commercial extracts like the 'soluble red woods,' Brazilwood and its allies.

Santalwood is the product of *Pterocarpus santalinus*, a papilionaceous tree growing in tropical Asia. It is imported from the East Indies, Ceylon, the coasts of Coromandel and Malabar, Golconda, Timor, Madagascar, &c. It occurs in commerce in the form of hard, heavy billets of a dull-red colour. In the state of powder it gives off a faint aromatic odour like that of orris root, specially noticeable when it is heated, or boiled with water. It yields to alcohol about 16 p.c. of colouring-matter (Pelletier), insoluble in cold water, sparingly soluble even in boiling water, but very soluble in alcohol, ether, acetic acid, and the caustic alkalis.

Barwood is the wood of a fine large tree *Baphia nitida*, and is imported from the west coast of Africa, *e.g.* Sierra Leone, Angola, &c. In the log its physical properties are generally similar to those of santalwood; in the rasped condition it has a somewhat brighter red colour, and it is devoid of aromatic odour. Boiling water extracts about 7 p.c. colouring matter, alcohol about 23 p.c., and hydrated ether about 19 p.c. (Girardin and Preisser). In caustic alkalis the colouring matter is readily soluble, with a reddish-purple colour, and is precipitated therefrom on addition of acids. Acetic acid gives a dark-brown coloured extract.

Camwood, stated by some to be derived from a variety of *Baphia nitida*, is a dyewood similar in general properties to those already mentioned, but somewhat more expensive and yielding deeper shades in dyeing. Its colouring matter seems to be present in larger amount, or it is more soluble than in the other woods. It is imported from the west coast of Africa, the Gaboon and Congo rivers, &c.

Caliatour-wood seems to be a somewhat more expensive variety of sanderswood, and possesses a similar aromatic odour. It is imported from the East Indies, and goes chiefly to the Continent.

The chemistry of these dyewoods is unsatisfactory, being incompletely studied, but from our present knowledge concerning their application in dyeing, the useful colouring principles they contain are evidently very closely related to each other, and perchance identical.

Sandel-red is the name given to the red resinous colouring principle first obtained by Pelletier on the evaporation of an alcoholic extract of sanderswood.

Santalic acid or *santalin*, obtained by Meier, is probably a purer form of 'sandel-red.' It is prepared by extracting sanderswood with ether, and evaporating the solution to crystallisation. The impure product thus obtained is washed with water, dissolved in alcohol, and precipitated with an alcoholic solution of lead acetate. The precipitate is well washed with boiling alcohol, then suspended in alcohol, and decomposed by dilute sulphuric acid; the filtrate from the lead sulphate is then evaporated to crystallisation. Thus obtained, santalin forms minute red crystals (m.p. 104°C.), insoluble in water, but very soluble in alcohol with a blood-red colour; soluble also in ether with a yellow colour, which becomes red on exposure to air. It dissolves readily in acetic acid, also in concentrated sulphuric acid with a dark-red colour. In caustic alkalis it dissolves readily with a purple colour. The formulæ assigned to santalic acid are $C_{15}H_{14}O_5$ (Weyermann and Häffely), and $C_{16}H_{16}O_3$ (Pelletier).

Santalic oxide is a substance extracted by Meier along with the santalic acid by means of alcohol. By extraction with water he obtained other bodies, which were named *santalide*, *santaloïde*, *santalidide*, and *santaloïdide.* All these are amorphous resinous substances whose existence as distinct chemical individuals is very doubtful.

Bolley prepared the colouring matter of sanderswood by exhausting it with alcohol and precipitating the concentrated solution by addition of water; also by extracting the wood with dilute caustic alkali, precipitating with acid, dissolving the precipitate in alcohol, and precipitating the solution with water. From analyses of several samples of colouring matter prepared according to these two methods, Bolley concluded that the colouring matter exists in two states of oxidation, according as it is obtained from young and pale-coloured wood, or such as is old and dark coloured; prepared from the latter he found it to contain more oxygen and less hydrogen. He noted further that alkaline solutions of the colouring matter become darker coloured on exposure to air, evidently because oxygen is absorbed. Other observers have remarked that the freshly-cut young branches of sanderswood exhibit in their interior a yellow colour, which only becomes red on exposure of the sections to the atmosphere.

Wimmer states that santalin is accompanied by a brown-coloured bitter principle soluble in boiling water, also a brown resinous colouring matter, *santalidine*, more soluble in the various solvents than santalin, of which it appears to be an oxidation product.

Santal (probably a still purer form of Meier's santalin) was obtained by Weidel by extracting sanderswood with dilute caustic alkali, and neutralising the filtered solution with hydrochloric acid. The voluminous brick-red precipitate thus obtained was washed, dried, and extracted with ether. The dark-red ethereal solution was concentrated, mixed with alcohol, and then allowed to evaporate spontaneously, when almost colourless crystals of santal separated. These were purified by washing with a little alcohol and recrystallising. This method yielded about $1\frac{1}{2}$ grms. santal per pound of wood. Santal crystallises from hot alcohol as colourless, lustrous, iridescent, quadrangular plates, having the formula $2C_8H_6O_3 + 3H_2O$. It is insoluble in hot water, carbon disulphide, benzene, and chloroform, and only slightly soluble in alcohol and ether. It dissolves somewhat sparingly in ammonia, but very readily in dilute caustic potash and soda, with a pale-yellow colour which very rapidly becomes red on exposure to air. Further oxidation changes the colour to green, and finally to a dirty brown. Addition of calcium chloride to a pale-yellow alkaline solution precipitates the santal in an almost colourless condition, but it quickly becomes coloured. Its alcoholic solution assumes a red colour on addition of ferric chloride. In concentrated sulphuric acid santal dissolves with a lemon-yellow colour, which is changed to brown by the addition of manganese dioxide. Nitric acid gives an olive-coloured solution, from which water precipitates yellow flocks. With bromine santal yields a granular crystalline product slightly soluble in alcohol. When santal is fused with caustic potash till the melt no longer dissolves in water with a red colour, it yields protocatechuic acid. Weidel considers santal to be isomeric with, and probably closely related to, piperonal.

Santalin ($C_{14}H_{12}O_4$) was obtained in small quantity by Weidel, by the further and long-continued extraction with ether of the brick-red resinous precipitate, *sandelwood resin*, thrown down by acid from the above-mentioned alkaline extract of the wood. On evaporating the ethereal solution it was deposited as a red crystalline powder, having a green metallic lustre. It is insoluble in boiling water, very slightly soluble in ether and even in hot alcohol; in the latter with a red colour. In ammonia and the caustic alkalis it dissolves with a reddish-purple colour, from which calcium chloride precipitates a purple precipitate. In concentrated sulphuric acid it dissolves with an orange colour.

Weidel's santalin seems to be a purer form of the resinous colouring matters analysed by Bolley, Weyermann, and Häffely, and is probably produced during the oxidation of santal in alkaline solution. The dark-red of an alkaline solution of sandelwood resin is changed to a straw-yellow colour by boiling with sodium amalgam; the reduction product has, however, not been isolated in the pure state because of its sensitiveness to oxidation, whereby it partially becomes resinous again. Sandelwood resin when heated with zinc-dust yields a small quantity of an oily distillate in which no anthracene can be detected. Fused with caustic alkali, it yields pyrocatechol and resorcinol. Judging from its slight solubility in alcohol and its characteristic green metallic lustre, Weidel's santalin does not appear to be identical with the santalin or santalic acid of Meier.

Franchimont and Sicherer, by adopting a method similar to Meier's, but extracting in the first instance with alcohol instead of ether, boiling the product eventually obtained with hydrochloric acid, and crystallising from diluted alcohol, obtained from sanderswood, and more abundantly from caliatour-wood, an amorphous colouring matter $C_{17}H_{16}O_6$ (m.p. 104°-105°), apparently identical with santalic acid. It is readily soluble in alcohol, acetic acid, caustic and carbonated alkalis, sparingly soluble in ether, and insoluble in chloroform and carbon disulphide. Fused with caustic potash it yields acetic acid, resorcinol, and probably also protocatechuic acid and pyrocatechol, together with a minute quantity of a volatile product smelling like rosewood.

Heated to 180°C. with concentrated hydrochloric acid, it yields methyl chloride; alcohol dissolves from the residue in the tube a substance $C_5H_{10}O_5$, and leaves behind a lustrous black mass soluble in caustic alkalis; ether withdraws from the hydrochloric acid solution a substance crystallising in colourless needles. The same substance is obtained by diluting the hydrochloric acid with water and distilling. The distillate gives with bromine water a precipitate of lustrous needles; m.p. 81°C

When the original colouring matter is boiled with dilute nitric acid it yields oxalic acid and a yellow bitter substance, probably picric or styphnic acid. By oxidation in alkaline solution with potassium permanganate it yields a crystalline substance having a strong odour of vanillin, also oxalic and acetic acids.

Anderson extracted ground barwood with anhydrous methylated ether free from alcohol. At first the solution is dark red, but ultimately it becomes almost colourless. By spontaneous evaporation of the concentrated ethereal solution a small quantity of *baphic acid* is deposited in the form of tabular crystals. After further evaporation, mixing the concentrated extract with alcohol, and allowing to stand for some days, there is deposited a crystalline magma of *baphiin* contaminated with a solid red colouring matter and some dark viscous colouring matter not yet examined.

After exhaustion with ether the wood is extracted with alcohol, and after highly concentrating the solution it is left at rest for some time, when it congeals to a semi-crystalline mass which contains a viscous red colouring matter and a crystalline constituent not examined.

Benzene and carbon disulphide at 100°C. are not such suitable solvents as ether, since they extract very little of the colourless substance baphiin, although they have the advantage of dissolving but mere traces of colouring matter, and the benzene also readily dissolves any baphic acid which may be present.

Baphiin $C_{24}H_{20}O_8$ (m.p. about 200°C.), crystallises from alcohol in the form of lustrous tabular crystals having an odour of orris root; from ether it crystallises in tufts of needles. It is insoluble in water, and very sparingly soluble in benzene and in carbon disulphide. In alcoholic solution it rapidly oxidises on exposure to air, producing orange-red or pale-purple colours. Possibly baphiin may prove to be identical with santal.

Baphic acid $C_{24}H_{22}O_9$ or $C_{24}H_{22}O_{10}$ is prepared by boiling baphiin with dilute caustic potash, and adding hydrochloric acid, when it is thrown down as a yellowish-white precipitate. Crystallised from ether it forms white nacreous scales, very soluble in ether, slightly less so in alcohol, and insoluble in water.

Baphinitin $C_{24}H_{24}O_6$ is thrown down as a crystalline precipitate on the addition of water to the filtrate from the precipitate of lead baphate which is formed on mixing alcoholic solutions of baphiin and lead acetate. It is also the chief product of the action of boiling dilute caustic potash on baphiin. Baphinitin forms white needles, soluble in alcohol and in ether, but insoluble in water; it has the same odour as baphiin but stronger.

Baphinitone $C_{26}H_{26}O_6$. On boiling baphiin with a strong aqueous solution of caustic potash without access of air, an insoluble residue is left which contains three substances: (1) baphinitin, moderately soluble in alcohol and ether; (2) baphinitone, very readily soluble in these liquids; (3) a small quantity of an unexamined substance, m.p. 164·1°C., very sparingly soluble even in hot alcohol, and separating therefrom in granular crystals. Baphinitone is extracted from the above-mentioned residue insoluble in caustic potash, by treating it with cold alcohol in which it readily dissolves along with a very small amount of baphinitin. The solution is evaporated, and the treatment with alcohol is repeated till the crystals thus obtained, after drying over sulphuric acid, have a melting-point of about 88°C. Baphinitone crystallises from alcohol in hemispherical masses composed of white lustrous radiating crystals insoluble in water.

Tribromo-baphinitone $C_{26}H_{23}Br_3O_6$ is obtained by mixing ethereal solutions of baphinitone and bromine; on evaporating off the ether it remains as a white substance, which may be purified by washing with alcohol or ether, in which it is almost insoluble. It separates from a hot ethereal solution in small granules, which melt with sudden blackening at 180·2°C.

Baphiin, baphinitone, and substance (3) above referred to, are all coloured orange-yellow by sulphuric acid; with nitric acid an orange-red colour is obtained, which changes gradually to green.

In addition to the above-mentioned substances, barwood contains, according to Anderson, at least three colouring matters. Ether extracts from the wood two of these: one (*a*) which is less soluble, and which tenaciously adheres to the baphiin, and another (*b*) which is more soluble and easily removed from it. When the extraction with ether is completed, alcohol will dissolve out a third colouring matter (*c*). All are insoluble in benzene, and give purple lakes with lead acetate, and purple solutions with alkalis.

The solubility in ether of the colouring matter (*a*), which is a bright-red powder, diminishes after exposure to air. Any adhering baphiin is removed from it by means of boiling benzene. The colouring matter (*b*) is crystalline, and dissolves readily in boiling alcohol; if hydrochloric acid be added to the solution the colour becomes darker, if then ammonia or caustic potash be added the colour changes to deep pink, whereas the final colour of the solution of the colouring matter (*c*) under similar treatment is deep purple.

Pterocarpin $C_{20}H_{16}O_6$ is a crystalline substance, apparently different from Weidel's santal, obtained by Cazeneuve and Hugounenq from sandelwood, to the amount of about 0·1 p.c., as follows. The rasped wood mixed with one-fourth its weight of slaked lime is made into a paste with water, then dried and extracted with ether containing alcohol. On evaporating the solution a crystalline deposit is obtained, which, when recrystallised from ether yields a mixture of platy crystals of *Pterocarpin* and long needles of *Homopterocarpin*, only the latter of which dissolves readily in carbon disulphide. Pterocarpin, m.p. 152°, is insoluble in water, also in acids and alkalis; it is soluble in cold, better still in hot alcohol, but is only sparingly soluble in ether. It crystallises from chloroform in hemihedric klinorhombic prisms, and turns the polarised ray to the right. It appears to be a lower homologue of homopterocarpin.

Homopterocarpin $C_{24}H_{24}O_6$, m.p. 82–86°C., is little soluble in cold alcohol. It turns the polarised ray to the left. Caustic potash has no action upon it, but heated with hydrochloric acid in sealed tubes to 120°C. it yields methyl chloride and resorcinol ether $(C_6H_4.OH)_2O$. When boiled with fuming nitric acid it yields oxalic acid and two trinitro-orcinols, of which one forms yellow needles, m.p. 162°C., the other is liquid. With excess of bromine homopterocarpin yields leafy crystals of $C_{21}H_{18}Br_6O_6$, m.p. about 270°C., and with 2 mols. bromine to 1 mol. homopterocarpin dissolved in chloroform colourless crystals of $C_{21}H_{23}BrO_6$ are obtained. The authors believe that homopterocarpin contains a kind of poly-orcin

$$(3[C_7H_5(OCH_3)(OH)_2]-3H_2O).$$

Pterocarpin in carbon disulphide solution gives with 2 mols. bromine a derivative

$$C_{20}H_{15}BrO_6,$$

m.p. 93°C., crystallising from benzene alcohol in yellowish needles.

A. Zander (1886) patented a method of rendering soluble the colouring matter of sanderswood and its allies, by treating the resinous colouring matter in the cold with fuming sulphuric acid, until a sample of the mixture dissolves in water, from which the new colouring matter is precipitated by means of common salt. The method does not appear to have any practical value.

Employment in dyeing.—In India it is said that sanderswood, with the addition of one-tenth of its weight of sapanwood, is employed in dyeing silk and cotton. In Europe, however, these dyewoods are never used in silk dyeing, but chiefly in the dyeing of wool, and occasionally cotton, for which latter barwood is exclusively employed.

In wool-dyeing various shades of brown are obtained by first boiling the wool in a bath containing the ground dyewood for one to one-and-a-half hours and then adding to the same bath a solution of one or other of the following mordants: potassium bichromate, ferrous sulphate, copper sulphate, alum. During the first part of the operation, termed 'stuffing,' the wool absorbs a considerable amount of the resinous colouring matter and thus acquires an orange or reddish-brown colour; during the second part, this combines with the metallic oxide or mordant, and in the case of the three first-mentioned metallic salts the colour is changed to a very dark brown. Hence this part of the operation is termed the 'saddening.' The same results are more rationally obtained by employing two separate baths, since then the unexhausted baths may be replenished and used again. If the mordanting operation precedes the boiling with dyewood, similar but less intense, and not such level, shades are obtained. By adding logwood, fustic, and other dyewoods along with the sanderswood, &c., a variety of browns, olives, &c., may be obtained.

So-called 'sour-browns' are obtained by boiling the wool in a bath containing sulphuric acid, sodium sulphate, camwood, &c., turmeric, and indigo extract, or some acid aniline blue. In this case, since no mordant is employed, the camwood merely imparts a comparatively pale orange or reddish brown to the wool, as above stated, which is modified and changed to a dark brown by the blue and yellow dyestuffs also employed. The above mode of using camwood, in order to furnish the red part of the compound shade ultimately obtained, is very irrational.

In dyeing vat-indigo blues on wool, sanderswood and barwood are commonly employed for the purpose of 'bottoming.' Before or after dyeing in the vat, but usually before, the woollen material is boiled in a bath containing the barwood or sanderswood; occasionally, the wool is mordanted. The object of the dyer is to impart a purplish hue to the indigo blue, thereby to intensify the colour somewhat, and to cause the colour to be less liable to rub off, or to wear gray at the seams in the case of clothing. The two latter points may probably be gained just as well by merely boiling the wool in water only, previous to dyeing in the vat. In this manner the wool is equally well softened and rendered more absorbent, so that the vat solution penetrates the fibre more thoroughly, and thus the precipitated indigo ultimately formed is inclosed within the substance of the fibre, and not so apt to rub off. The utility of the presence of the barwood in the bath, except for the purpose of modifying the shade of blue, is very questionable indeed.

Barwood-red on cotton, also called sometimes 'mock Turkey red,' is a bluish red of medium brilliancy. It is produced by first working the cotton in a cold decoction of tannin matter—*e.g.* sumach—then mordanting it by working in a cold weak solution of stannic chloride or nitromuriate of tin, and, after washing, boiling in a bath with ground barwood.

All the colours produced from these dyewoods, whether on wool or cotton, are not fast to light. Those obtained on wool with the use of mordants are fast to milling; although the colours do not 'bleed,' alkalis tend to alter the hue of the colours and to render them more purplish.

At the present time these dyewoods are being rapidly superseded by the alizarin colours.

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SANDIVER. (Fr. *Suint de verre.*) The scum formed on the surface of the molten glass in the glass pots; known also as *glass gall* (*v.* GLASS).

SANDSTONE. (*Grès*, Fr.) A granular siliceous rock, consisting of consolidated sand. If the cohesion is imperfect, the friable mass is sometimes known as *sand-rock*. The consolidation of the sand may be effected either by pressure, or by deposition of mineral matter forming an agglutinating medium between the grains. When the cement is siliceous, the resulting rock has great hardness and durability, but is difficult to work. Where the grains of sand are united by calcium carbonate, a *calcareous sandstone* is produced; such a rock may be readily worked as a freestone, but by weathering it is apt to lose the calcareous cement, and, becoming more or less cavernous in texture, tends to suffer disintegration. In an *argillaceous sandstone* the cement is clayey, and the stone is not generally durable as a building material. In a *micaceous sandstone* scales of mica are present, and in many cases facilitate the splitting of the stone along the planes of bedding, as in the Yorkshire flagstone. A *felspathic sandstone* contains grains of felspar, either crystalline or more or less kaolinised: much of the millstone grit of England is of this character, having clearly resulted from the disintegration of granitic rocks. The term *arkose* is often applied to a sedimentary rock made up of the constituent minerals of granite, rearranged by deposition in water.

Many sandstones—especially those of the Old Red Sandstone, the Permian, and the Trias—present various tints of red and brown, due to the presence of ferric oxide, or its hydrate, acting as a cement, and forming a thin pellicle around each grain of quartz. Green sandstones, such as those of the upper greensand of Surrey, owe their colour to dark grains of glauconite, generally the internal casts of the chambers of foraminifera. The bluish and greyish tints of many sandstones are referred to the presence of ferrous carbonate, or of finely-divided iron pyrites, or even to iron phosphate. Sandstones which are 'blue hearted' usually assume yellow or brown tints where exposed to oxidising influences. Grains or crystals of iron pyrites in a sandstone are apt to produce rusty blotches when weathered. (On the colour of sandstones *v.* G. Maw, Quart. Journ. Geol. Soc. 24, 1868, 351.)

If the component grains of silica are sharp, the rock is termed a *grit*; many grits are valued as grindstones, while if very fine in texture they may sometimes be used as whetstones. A coarse grit, with large grains of quartz, may be employed as a millstone.

It has been shown by F. Clowes (C. N. 52, 1885, 194) that in certain Triassic sandstones, like the 'hemlock stone,' near Nottingham, the grains of sand are united by barium sulphate. Certain sandstones are impregnated with metallic compounds, rendering them useful as ores: thus, the lower keuper sandstones of Alderley Edge and of Mottram St. Andrew's, in Cheshire, have yielded copper carbonates, both green and blue, with galena and cerussite, cobalt and manganese ores, and vanadinite. The workable part of the metalliferous sandstone contained an average of 1·4 p.c. of copper; this was dissolved out by dilute hydrochloric acid, and precipitated by scrap iron (Greenwell, Proc. S. Wales Inst. Eng. 4, 1866, 44; Hull, Geol. Mag. 1, 1864, 65). Native copper is disseminated in a granular form through certain sandstones at Lake Superior. The bunter sandstone, near Commern, in the Eifel, contains valuable deposits of lead-ore, usually sulphide, though sometimes carbonate, occurring in nodules, whence the rock is termed *Knottensandstein.* Many iron ores of the secondary rocks, like those of Northamptonshire and Lincolnshire, are so siliceous as to pass into highly ferruginous sandstones. (For analyses of sandstones, *v.* J. A. Phillips, Quart. Journ. Geol. Soc. 37, 1881, 21; for American sandstones *v.* G. P. Merrill, Smithson. Rep. for 1886, part 2, 443). F. W. R.

SANGUINARIA. *Bloodroot.* The rhizome of *Sanguinaria canadensis* contains an alkaloid, *Sanguinarine* $C_{17}H_{15}NO_4$, said to be identical with *Chlererythrine*, obtained from celandine (*Chelidonium majus*) (*v.* Naschold, J. pr. 106, 385).

SANIDINE *v.* FELSPAR.

SANTALIC ACID. *Santalin v.* SANDERSWOOD.

SANTAL OIL, which is obtained by the distillation of the sandelwood of Bombay (*Santalum album*) with steam, was formerly only made use of in perfumery, but it is now also used in medicine in place of copaiba balsam. The yield from 100 kilos. of wood amounts to from 1·25 to 2·80 kilos. This oil is a rather thick fluid of sp.gr. 0·945 at 15°. It boils at from 300° to 340°, and consists almost entirely of two oxidised oils $C_{15}H_{24}O$ and $C_{15}H_{26}O$, which boil at 300° and 310° respectively. The former is present in greater abundance than the latter. By the action of phosphoric anhydride these oils are converted into the compounds $C_{15}H_{22}$ and $C_{15}H_{24}$ respectively, which boil at 245° and 260°. Oil of cedarwood, when freed from its oxidised constituents, possesses almost exactly the composition of the hydrocarbon $C_{15}H_{22}$, and boils at the same temperature. The two products are therefore probably identical. The hydrocarbon $C_{15}H_{24}$ is isomeric or identical with copaiba oil. By slow distillation sandelwood oil yields two products, boiling respectively below 250° and above 350°. Water and hydrogen are at the same time formed. The reaction is, however, incomplete, but on heating in a closed vessel at 310°, the following reactions take place:

$$4C_{15}H_{24}O = C_{20}H_{30}O + C_{40}H_{62}O_3 + 4H$$
$$C_{10}H_{62}O_3 = C_{10}H_{60}O_2 + H_2O.$$

The oil $C_{20}H_{30}O$ boils at 240°, and is converted by phosphoric anhydride into the hydrocarbon $C_{10}H_{14}$, boiling at 175° to 180°, and smelling of cymol. The product $C_{40}H_{62}O_3$ is liquid, and distils over at 340°, while $C_{40}H_{60}O_2$ is found in the fraction boiling above 350°; it possesses the consistency of honey. The oil $C_{15}H_{26}O$ so behaves under the influence of heat that among the decomposition products of sandelwood oil are found liquids which boil from 240° to 260°, and hydrocarbons produced by dehydration, boiling between 185° and 200°. By the action of glacial acetic acid on sandelwood oil at 150° is obtained, after seven or eight hours, a fluid boiling between 280° and 300°. This is a mixture of two products, of which one boils between 280° and 285°, and the other at 298°. The first $C_{30}H_{46}O$, is formed from $2C_{15}H_{24}O$ by the loss of H_2O; the second is the acetic ether, $C_{17}H_{28}O_2$, of the oil $C_{15}H_{26}O$. It possesses an agreeable fruity odour. Hydrochloric acid yields at 125° the hydrochloric ether of sandelwood oil, which boils at 275°. The reaction is more complicated than with acetic acid. These last reactions confirm the composition of sandelwood oil above given. They show, moreover, that the oil $C_{15}H_{26}O$ possesses the characters of an alcohol. As regards the second oil $C_{15}H_{24}O$, which approaches an aldehyde in its properties, it is probable that it is the aldehyde of the alcohol $C_{15}H_{26}O$ (S. C. I. 1, 336).

SANTALOL *v.* CAMPHORS.

SANTONICA. *Wormseed.* (*Semen-contra*, Fr.; *Wurmsamen*, Ger.) The so-called wormseed consists of the minute unexpanded flower-heads of *Artemisia maritima*, variety *Stechmanniana* (Besser) (*v.* Bentl. a. T. 157). The species is widely distributed throughout Europe and Asia; but the variety which yields the more esteemed Levant wormseed of commerce is for the most part confined to southern Russia and Turkestan, especially the district of the lower Volga. Thence the drug enters European markets by way of Nijni Novgorod. The santonica shrub evolves a marked camphoraceous odour, which is distinctly perceived in the drug itself when rubbed. The taste is bitter and aromatic (*cf.* Flückiger, Ph. [3] 17, 449).

Santonica is used in medicine almost exclusively for its powerful anthelmintic property in the case of the round lumbricoid worm *Ascaris lumbricoides*; but for this purpose its chief active constituent, santonin, has quite superseded the drug itself. When santonin or santonica has been administered the urine assumes a saffron-yellow colour, changed to violet by alkalis, and in many cases the field of vision is suffused with a yellow hue. König finds that the visual power of recognising the ulterior portion of the blue and the entire extent of the violet of the solar spectrum is entirely abolished for the time being, whilst the point of neutrality is situated at the rare length of 573, this being the exact complementary point of the suppressed violet. König infers that the visual phenomena, occasioned by the ingestion of sodium santoninate, do not constitute actual violet blindness, the retina or optic nerve being affected, but that the rays of violet light are, during the santoninic toxical condition, simply absorbed by certain of the media of the eye, which have been abnormally, and, of course, only temporarily, affected in that direction by the drug (S. C. I. 1889, 566).

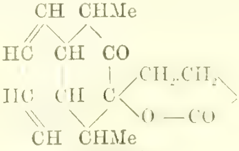
The well-known crystalline compound *santonin*, $C_{15}H_{18}O_3$, was discovered in santonica by Kahler in 1830 (Brandes, Arch. 34, 318; 35, 216), and independently obtained immediately afterwards by Alms (Brandes, Arch. 34, 319; 39, 190). It was further studied by Trommsdorff (A. 11, 190) and by Heldt (A. 63, 10); also by Oberdörffer (Brandes, Arch. 35, 319), Guillemette (J. Ph. 26, 152), Roder (Jahrb. pr. Pharm. 6, 45), Miahle and Calloud (J. Ph. [2] 4, 387), and Cerutti (Ar. Ph. [2] 52, 148). To obtain it the method adopted by the British Pharmacopœia of 1885 may be employed. This is essentially the process of Calloud (J. Ph. [2] 15, 106). The drug is extracted by digestion with lime and water, and from this solution, after suitable concentration and acidification, the santonin in an impure form slowly precipitates. It has then to be purified by washing with water and dilute ammonia, and by treatment with animal charcoal, and finally, it is dissolved in alcohol and crystallised from that solvent. The crystallisation has to be effected in a dark place, otherwise the product is converted by the actinic rays into a yellow compound, which, at least in those cases where the alcohol is not free from water, is the ethyl ether of a new dibasic acid *photosantonic acid* $C_{15}H_{22}O_5$ (Sestini, G. 6, 357). The yield of santonin varies from 1 to 2 p.c. For the preparation of santonin, see also Busch (J. pr. [2] 35, 322) and Cech (D. P. J. 253, 474).

Methods which are modifications of the process just described are also employed in the valuation of specimens of the drug by Dragendorff (Ar. Ph. 1878, 306) and Flückiger and Ehlinger (Ar. Ph. [3] 24, 1). The following process is given by Flückiger and Ehlinger:—5 parts of wormseed and 1 part of milk of lime are boiled for two hours in a considerable quantity of dilute alcohol, and the liquid poured off after cooling; this treatment is repeated twice, the extracts are mixed, and the alcohol removed by distillation. The residual liquid is then saturated in the cold with carbonic acid, the mixture, after standing some hours, filtered, and the filtrate evaporated to dryness. The residue is triturated with animal charcoal and alcohol (sp. gr. 0·935), and the paste mixed with more alcohol is heated to boiling. The whole is then thrown on a filter, the residue washed with hot alcohol, and the filtrate concentrated by evaporation, when, after standing for some hours, the santonin separates in crystals and may be dried and weighed (Flückiger, Ph. [3] 17, 449).

Santonin crystallises from water in flattened hexagonal prisms and from ether in rhombic plates. It melts at 170° (Schmidt, Z. 1865, 320; Leroy, R. P. 1878, 104), and when heated to a higher temperature in small quantities it may be sublimed. It is nearly insoluble in water; but is soluble in ether, and more so in alcohol and chloroform (*cf.* Trommsdorff; Schlimpert, Ar. Ph. [2] 100, 151). The alcoholic solution is strongly lævorotatory (Buignet, J. Ph. [3] 40, 252; Hesse, A. 176, 125). If a small fragment of santonin be dissolved in cold sulphuric acid and a drop of ferric chloride solution be added, there is developed a beautiful crimson colour which passes over to purple and violet (Lindo, C. N. 36, 222; Knopp, D. P. J. 268, 42). A crimson colour is also obtained when santonin is treated with alcoholic potash (Heldt). When heated with dilute acids sugar is not formed (Schmidt, Z. [2] 1, 212).

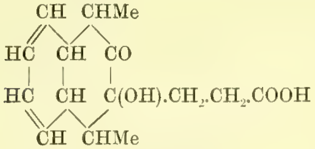
Halogen derivatives were obtained from santon in by Heldt (A. 63, 32) and by Sestini (Bl. 5, 202), and it is shown to form definite addition compounds with metallic oxides. *Monochlorosantonin* $C_{15}H_{17}ClO_3$, *dichlorosantonin* $C_{15}H_{16}Cl_2O_3$, and *trichlorosantonin* $C_{15}H_{15}Cl_3O_3$ were prepared, and metallic compounds having the general formula $C_{15}H_{18}O_3,M'_2O$. The compound with sodium consists of large rhombic prisms. These metallic compounds were proved by Hesse (B. 6, 1280) to be combinations of a new acid of which santonin is the anhydride, and not to be salts of santonin, as was at first supposed. This new *santoninic acid* $C_{15}H_{20}O_4$ is obtained when the sodium compound of Heldt is treated with a mineral acid. Its salts, the santoninates, are formed by the addition of a molecule of a metallic oxide to a molecule of the anhydride, santonin. The free acid may also be easily reconverted into santonin by the removal of the elements of water. This is accomplished by simply heating it to 120°, or by treatment with concentrated sulphuric acid. Santoninic acid consists of colourless granular crystals which are unaffected by sunlight.

By the prolonged application of heat and by the action of reagents Cannizzaro and some of his pupils have brought to light a large number of isomerides of santoninic acid and its anhydride, santonin, and other related compounds, and from each of these have obtained derivatives. This work has indeed been carried so far that Cannizzaro has ventured to put forward the following structural formula for santonin. It is represented as a derivative of naphthalene and as an inner anhydride or lactone of santoninic acid:



Santonin.

The corresponding formula for santoninic acid is:



Santoninic acid.

See Cannizzaro and Sestini (G. 3, 241); Cannizzaro (G. 4,452; 6,341; 6,355; 13, 385; B. 18, 2,746); Cannizzaro and Amato (B. 7, 1103); Struever (G. 6, 349); Sestini (G. 6, 148*a*, 357); Cannizzaro and Valente (G. 8, 309); Cannizzaro and Carnelutti (G. 8, 318; 10, 459; 10, 461; 12, 393; B. 12, 1574; 13, 1516); Villavecchia (B. 18, 2859); Cannizzaro and Fabris (B. 19, 2260); Gucci (G. 19, 367); Grassi-Cristaldi (G. 19, 382); Wagner (B. 20, 1662). For the physiological action of santonin derivatives, many of which have been used in medicine, see Coppolo (C. J. 54, 310).

Santonica contains, besides santonin and the substances found in all plants, certain volatile constituents. When distilled with steam 1 to 2 p.c. of a *volatile oil* passes over, which boils at 175°, and is composed for the most part of *cineol* $C_{10}H_{18}O$, which boils at 176°, and which readily loses water with formation of *cinene* $C_{10}H_{16}$ and *dicinene* $C_{20}H_{32}$ (Wallach, A. 245, 195); Hell a. Stürcke, B. 17, 1971). See also Kraut (J. 1862, 460); Kraut and Wahlforss (A. 128, 293); Wallach and Brass (A. 225, 291); Wallach and Gildmeister (A. 246, 268); Brühl (B. 21, 461). A. S.

SANTONIN *v.* SANTONICA.

SANTONINIC ACID *v.* SANTONIN.

SAPAN-WOOD *v.* BRAZILWOOD. The export of this valuable dye-wood from Bangkok has decreased each year since 1884, when the export was 3,079 tons. In 1887 it fell to 1,772 tons, and in 1888 to 1,372 tons. The sapan-wood forests are, it appears, much exhausted, and without forest regulations there is danger of the wood ceasing to be an article of export. The supply from the Raheng district, whence most of the wood formerly came, has now almost ceased, and that which finds its way to Bangkok is derived chiefly from the Lakhon forests, the trees being torn up by the roots and floated down by way of Raheng to Bangkok. Most of the sapan-wood shown in the returns is exported in the form of dunnage with rice cargoes (S. C. I. 9, 985).

SAPONIN *v.* SENEGA.

SAPPHIRE *v.* ALUMINIUM; also CORUNDUM.

SARCINE *v.* HYPOXANTHINE.

SARDONYX *v.* AGATE.

SARSAPARILLA. (*Radix sarsæ*; *Racine de Salsepareille*, Fr.; *Sarsaparillwurzel*, Ger.) Of the various kinds of sarsaparilla imported into this country that variety which originally came by way of Jamaica, and is still known as 'Jamaica sarsaparilla,' is alone recognised by the British Pharmacopœia. It was formerly believed to be the root of *Smilax officinalis* (Kunth; Bentl. a. T. 289), but recent observations on a flowering specimen at Kew indicate that the official drug is derived from a distinct species to which Sir J. Hooker gives the name *S. ornata* (Ph. [3] 19, 989). It is a woody climbing plant which inhabits Central America, especially on the mountains known as the Cordillera of Chiriqui, in the isthmus of Panama, adjoining Costa Rica, and perhaps other districts in the northern parts of South America. For botanical and other characters, see Pereira (Mat. Med. 3rd ed. 1153) and Fl. a. H. 703. Sarsaparilla is an alterative medicine, employed especially in the treatment of some forms of syphilis, but it is not regarded with the same favour that it was formerly.

Of the constituents of sarsaparilla, with the exception of *starch*, which occurs to the greatest extent in some of the non-official varieties of the drug, the only ones to be described are a trace of *volatile oil* and the crystalline compound *parillin*. Little is known of the volatile oil. Pereira obtained only a few drops from the distillation of 140 lbs. of the root. This was heavier than water, was soluble in alcohol, and possessed the odour and acrid taste of sarsaparilla.

Parillin was discovered in sarsaparilla by Pallota in 1824 (Brugn. Giorn. 17, 386), who called it also 'pariglin.' Folchi soon afterwards obtained a similar substance, which he named 'smilacin'; similarly Thubeuf described 'salseparisin' (J. Ph. 18, 734; 20, 162 a. 679), and Batka 'parillinic acid' (A. 11, 313). Finally, Poggiale (J. Ph. 20, 553) proved that these various products were one and the same compound, and for this he adopted the name 'smilacin.' 'Sarsaparillin' is another name for the same substance. See also Buchner (R. P. 53, 1) and Petersen (A. 15, 74 a. 17, 166). Flückiger, however, having reinvestigated the subject, adopts the term 'parillin,' as originally employed by Pallota (Ar. Ph. [3] 7, 532; Ph. [3] 8, 488). Parillin is deposited in a crystalline form when an alcoholic extract of the root, after treatment with animal charcoal, is concentrated. When recrystallised from alcohol, it assumes the form of colourless needles. Flückiger precipitates the crude parillin from the concentrated alcoholic solution by the addition of water, and then purifies in the manner described. The yield was about 0·19 p.c. of the root employed. Air-dried parillin melts at 210°. Freed from water at 100°, it seems to have the formula $C_{40}H_{69}O_{18}$ or $C_{48}H_{85}O_{18}$. It is almost insoluble in cold, though somewhat soluble in hot, water; is soluble in alcohol and less so in chloroform. Dilute (10 p.c.) sulphuric acid when heated with parillin gives a green colour, which on further concentration changes to red and brown. It is a glucoside, yielding by the action of dilute acids *sugar* and *parigenin*. The latter compound was obtained by Flückiger in scaly crystals from its solution in alcohol. It is distinguished from parillin by being quite insoluble even in hot water. Parillin and parigenin seem nearly related to saponin and sapogenin, if not also to cyclamin and cyclamiretin. A. S.

SASSAFRAS OIL *v.* OILS, ESSENTIAL.

SAVINE, OIL OF, *v.* OILS, ESSENTIAL.

SAXON BLUE. A term occasionally applied to a solution of indigo in sulphuric acid. Used also as a synonym for smalt.

SAXON GREEN. *Emerald green v.* PIGMENTS.

SCAMMONY *v.* GUM RESINS.

SCANDIUM *v.* CERIUM METALS.

SCAPTIN *v.* Digitalis.

SCARLET, ATLAS, *v.* Azo- colouring matters.

SCARLET, BIEBRICH, *v.* Azo- colouring matters.

SCARLET, BRILLIANT, *v.* Azo- colouring matters.

SCARLET, COCHINEAL, *v.* Azo- colouring matters.

SCARLET, CROCEÏN, *v.* Azo- colouring matters.

SCARLET, DOUBLE, *v.* Azo- colouring matters.

SCARLET OCHRE. *Venetian red* *v.* Pigments.

SCARLET, WOOL, *v.* Azo- colouring matters.

SCARLET, XYLIDINE, *v.* Azo- colouring matters.

SCHEELE'S GREEN *v.* Arsenic.

SCHEELITE, SCHEELINITE, *v.* Tungsten.

SCHLIPPE'S SALT. *Sodium sulphantimonate* *v.* Antimony.

SCHORLOMITE *v.* Titanium.

SCHULTZE'S POWDER *v.* Explosives.

SCHWATZITE *v.* Fahl-ore.

SCHWEINFURTH GREEN. *Emerald green* *v.* Arsenic; also Pigments.

SCHWEITZER'S REAGENT. A solution of hydrated cupric oxide in ammonia, used as a solvent for cellulose (*v.* Cellulose).

SCILLA, SCILLAIN, SCILLIN, SCILLIPICRIN, SCILLITIN, SCILLOTOXIN, *v.* Squill.

SCLERO - CRYSTALLINE, SCLEROERYTHRIN, SCLERIODIN, SCLEROMUCIN, SCLEROXANTHIN, SCLEROTIC ACID *v.* Ergot of rye.

SCOPARIN *v.* Broom tops.

SEALING-WAX. (*Cire à cacheter*, Fr.; *Siegellack*, Ger.) The Hindoos from time immemorial have possessed the resin lac, and were long accustomed to use it for sealing manuscripts before it was known in Europe. It was first imported from the East into Venice, and then into Spain; in which country sealing-wax became the object of a considerable commerce, under the name of Spanish-wax.

If shellac be compounded into sealing-wax immediately after it has been separated by fusion from the palest qualities of stick or seed lac, it then forms a better and less brittle article than when the shellac is fused a second time. Hence sealing-wax rightly prepared in the East Indies deserves a preference over what can be made in other countries, where the lac is not indigenous. Shellac can be restored in some degree, however, to a plastic and tenacious state by melting it with a very small portion of turpentine. The palest shellac is to be selected for bright-coloured sealing-wax, the dark kind being reserved for black.

The following proportions may be followed for making red sealing-wax. Take 4 ounces of shellac, 1 ounce of Venice turpentine, and 3 ounces of vermilion. Melt the lac in a copper pan suspended over a clear charcoal fire, then pour the turpentine slowly into it, and soon afterwards add the vermilion, stirring briskly all the time of the mixture with a rod in either hand. In forming the round sticks of sealing-wax, a certain portion of the mass should be weighed while it is ductile, divided into the desired number of pieces, and then rolled out upon a warm marble slab, by means of a smooth wooden block, like that used by apothecaries for rolling a mass of pills. The oval sticks of sealing-wax are cast in moulds, with the above compound in a state of fusion. The marks of the lines of junction of the mould-box may be afterwards removed by holding the sticks over a clear fire, or passing them over a blue gas-flame. Marbled sealing-wax is made by mixing two, three, or more coloured kinds of it while they are in a semi-fluid state. From the viscidity of the several masses, their incorporation is left incomplete, so as to produce the appearance of marbling. Gold sealing-wax is made simply by stirring gold-coloured mica spangles into the melted resins. Wax may be scented by introducing a little essential oil, essence of musk, or other perfume. If 1 part of balsam of Peru be melted along with 99 parts of the sealing-wax composition, an agreeable fragrance will be exhaled in the act of sealing with it. Either lampblack or ivory-black serves for the colouring matter of black wax. Sealing-wax is often adulterated with resin; in which case it runs into thin drops at the flame of a candle.

The following proportions are stated to form good sealing-wax:—

Red, No. 1.—4 oz. Venetian turpentine, 6 oz. shellac, $\frac{3}{4}$ oz. colophony, $1\frac{1}{4}$ oz. cinnabar, &c.

Red, No. 2.—4 oz. turpentine, $5\frac{1}{2}$ oz. shellac, $1\frac{1}{2}$ oz. colophony, $1\frac{1}{4}$ oz. cinnabar, magnesia to colour.

Fine black.—$4\frac{1}{2}$ oz. Venetian turpentine, 9 oz. shellac, $\frac{1}{2}$ oz. colophony, lampblack mixed with oil of turpentine as much as is required.

Black.—4 oz. Venetian turpentine, 8 oz. shellac, 3 oz. colophony, lampblack, and oil of turpentine.

Yellow.—2 oz. Venetian turpentine, 4 oz. shellac, $1\frac{1}{4}$ oz. colophony, $\frac{3}{4}$ oz. King's yellow.

Dark brown.—4 oz. Venetian turpentine, $7\frac{1}{2}$ oz. shellac, $1\frac{1}{2}$ oz. brown English earth (ochre).

Light brown.—4 oz. Venetian turpentine, $7\frac{1}{2}$ oz. shellac, 1 oz. brown earth, $\frac{1}{2}$ oz. cinnabar.

Dark blue.—3 oz. Venetian turpentine, 7 oz. fine shellac, 1 oz. colophony, 1 oz. mineral blue.

Green.—2 oz. Venetian turpentine, 4 oz. shellac, $1\frac{1}{4}$ oz. colophony, $\frac{1}{2}$ oz. King's yellow, $\frac{1}{4}$ oz. mountain blue.

Gold.—4 oz. Venetian turpentine, 8 oz. shellac, 14 sheets of genuine leaf-gold, $\frac{1}{2}$ oz. bronze, $\frac{1}{2}$ oz. magnesia with oil of turpentine (Ure).

SECRETAGE. A process in which mercury or some of its salts is employed to impart to the fur of animals the property of felting (Ure).

SECURITE *v.* Explosives.

SEED LAC *v.* Resins.

SEIGNETTE'S SALT. (*Potassium sodium tartrate* $C_4H_4O_6KNa.4H_2O$ or *Rochelle salt.*) So named from having been discovered by Seignette, an apothecary in Rochelle, in 1672.

SELENITE. *Hydrated calcium sulphate* (*v.* Calcium; also Cements).

SELENIUM. Symbol Se. At. wt. 78·87 (Petterssen and Ekman). This element is widely distributed in small quantities. It occurs native in cavities in Vesuvian lavas. In combination it is found as *sulphur selenide* or *selensulphur* in native sulphur; as *clausthalite* PbSe, *lehrbachite* PbSeHgSe, *onofrite* HgSe4HgS, *eucairite* $CuSeAg_2Se$, *crookesite* (CuTlAg)Se, and other minerals. It occurs in many varities of copper and iron pyrites, especially in Norwegian pyrites, and is precipitated from the sulphuric acid prepared from them. It has been found by H. N. Warren in meteoric iron.

Selenium is prepared from the deposit from sulphuric acid in the chambers and Glover's towers. The deposit is boiled with two parts of sulphuric acid (diluted with an equal volume of water) with the addition of nitric acid or potassium chlorate, until the red colour has disappeared. The solution, which contains selenic acid, is heated with one-half its volume of fuming hydrochloric acid and evaporated to one-quarter, chlorine being evolved and selenious acid remaining. The solution is then saturated with sulphurous oxide, and the precipitated selenium, which contains lead, copper, and other metals, is fused with potassium nitrate and potassium carbonate, and the potassium selenate produced is dissolved out and re-treated with hydrochloric acid and sulphurous oxide.

By a second method the chamber deposit is heated with concentrated potassium cyanide solution until it becomes grey. The solution, containing potassium selenocyanate, is filtered and treated with hydrochloric acid and sulphurous oxide, the precipitated selenium being separated from metals as before.

Selenium is known in a form soluble in carbon bisulphide and an insoluble, or metallic, form. The soluble form is produced as a brick-red powder by precipitating cold selenious acid solution with sulphurous oxide, and as a black crystalline powder when deposited from a hot solution. From carbon bisulphide it crystallises out in dark-red crystals of 4·5 sp.gr. When heated it gradually softens, assuming the plastic condition; when melted and cooled quickly, it forms a black glossy mass, still soluble but of sp.gr. 4·28. If heated and cooled to 210°, and retained at about that temperature, it solidifies after a time; more slowly if kept at a temperature about 96°, forming a granular crystalline mass, the temperature rising to 217°. This form is almost insoluble in carbon bisulphide, and has a sp.gr. 4·5. If heated to about 168° the crystals become almost black, increasing in density to 4·8, and becoming quite insoluble in carbon bisulphide. This form may also be produced in microscopic crystals by exposure to the air of a concentrated solution of potassium or sodium selenide.

The crystalline form conducts electricity, its resistance increasing when heated but diminishing considerably on exposure to light, the action being principally produced by the red rays. The change of conductivity is instantaneous, and is almost doubled in sunlight, even the light from a small lamp having a noticeable effect. The resistance gradually returns after removal from light. According to Bidwell (C. N. 52, 191), the sensitiveness depends on the presence in the selenium of a metallic selenide. On this property depends the construction of the *photophone*, in which light is converted into electricity. A. Weinhold (D. P. J. 239, 160) describes the preparation of selenium resistance rods for photophonic purposes. Selenium has also been recently used for observations of the transit of Venus and of the sun's eclipse.

Selenium boils at 665° at 760 mm. (Troost), forming a dark-red vapour of anomalous density at temperatures near the boiling-point but normal at 1420°.

Selenium is odourless and tasteless, but the vapour possesses an odour of putrid horseradish. It burns with a reddish-blue flame. In cold concentrated sulphuric acid it dissolves with a fine green colour, with formation of selenosulphuric trioxide $SeSO_3$, from which solution selenium is precipitated by water. Selenium closely resembles sulphur. It mixes in all proportions with sulphur, crystals containing both elements in varying proportions being deposited from their solution in carbon bisulphide. Selenium can also replace sulphur in alums.

Seleniuretted hydrogen SeH_2 is produced by the action of dilute hydrochloric acid on ferrous or alkaline selenide or by heating selenium in hydrogen gas, the quantity produced depending in the latter case upon the temperature. It decomposes when heated, so that when selenium is heated in hydrogen in a glass tube the hydride is at first produced, and is again reduced with deposition of crystalline selenium on the colder parts of the tube. It is a colourless gas of persistent fœtid odour, more soluble in water than sulphuretted hydrogen, the solution being acid to litmus and absorbing oxygen from the air, with deposition of red selenium. It precipitates most heavy metals as selenides.

Selenium forms one oxide SeO_2, produced by heating selenium in dried oxygen, in white needle-shaped hygroscopic crystals, which sublime unmelted at about 300°, forming a yellow vapour.

Selenious acid H_2SeO_3 is produced by solution of selenium in nitric acid or of selenious oxide in hot water. It crystallises from solution in colourless prisms. A number of acid and neutral selenites are known. They all evolve selenium when heated with ammonium chloride in a tube, and produce the horseradish odour when heated on charcoal in the reducing flame.

Selenic acid H_2SeO_4 may be produced by the action of chlorine or bromine on aqueous selenious acid. When selenites are similarly treated, selenates are produced. It cannot be obtained in the anhydrous condition, as it decomposes into oxygen, water, and selenious oxide at 280°. Aqueous solution of this acid dissolves gold, copper, iron, and other metals. Selenates closely resemble sulphates; they are all reduced to selenites when heated with hydrochloric acid.

Acids containing both sulphur and selenium are also known, as selenosulphuric acid H_2SeSO_3 and selenotrithionic acid $H_2SeS_2O_6$.

Selenium forms two chlorides and an oxychloride Se_2Cl_2, Se_2Cl_4, $SeOCl_2$, and the corresponding iodides and bromides, an oxybromide and a fluoride. Two chlorobromides, $SeClBr_3$ and $SeBrCl_3$, and a biselenide of carbon CSe_2, resembling bisulphide of carbon, are also known.

SEMINA CONTRA OIL *v.* OILS, ESSENTIAL.

SEMINOSE. In many seeds the cell walls of the endosperm or the cotyledons are considerably thickened. In the case of some seeds it has been shown that this extra material serves as reserve food for the embryo, whilst in other instances this proof has not been forthcoming. The thickened cell walls consist either of amyloid or cellulose. R. Reiss has examined a number of those seeds which contain cellulose as reserve material. This cellulose differs considerably from ordinary cellulose. On hydrolysis with sulphuric acid, a dextrorotatory sugar is obtained. It reduces Fehling's solution, and is capable of fermentation. Reiss gives to it the name of *seminose*. It has not yet been obtained in the pure state, so that its properties are not accurately known, but it yields several readily crystallisable derivatives. Phenylhydrazine acetate mixed with an aqueous solution of seminose in the cold gives a very considerable precipitation of a colourless hydrazone. It is soluble in 80–100 parts of boiling alcohol of 50–60 p.c., but the greater part separates out again on cooling. It crystallises in small rhombic plates, melting at 185–186°C. It is composed of one molecule of $C_6H_{18}O_6$ united to one of phenylhydrazine with separation of one molecule of water. Its formula is $C_{12}H_{18}N_2O_5$. A neutral aqueous solution of seminose gives with basic acetate of lead a white gelatinous precipitate, soluble in excess of the reagent. Its composition is

$$PbO(C_6H_{12}O_6) + H_2O.$$

Seminose readily yields an isonitroso- derivative in colourless crystals of the formula $C_6H_{13}O_6N$. It is fairly soluble in water, and melts at 176°C. with blackening. These facts conclusively prove that seminose is a distinct sugar. The formation of seminose is easily detected by the insolubility of its phenylhydrazone, which is a ready means of distinguishing the reserve food cellulose from ordinary cellulose and amyloid. Seminose was obtained from the following families of plants:—Palmaceæ, liliaceæ, iridaceæ, loganiaceæ, and rubiaceæ. Seeds containing amyloid as reserve food do not give seminose on hydrolysis. (R. Reiss, B. 22, 609–613; S. C. I. 8, 406.)

SENARMONTITE. *Antimony sesquioxide v.* Antimony.

SENECA OIL. A name given to American petroleum, from the circumstance that it was collected by the Seneca Indians.

SENEGA ROOT. *Seneka Snake Root. Senegæ Radix.* (*Racine de Polygala de Virginie*, Fr.; *Senegawurzel*, Ger.)

The root of *Polygala Senega* (Linn.; Bentl. a T. 29), a plant inhabiting the central and northern portions of North America. It is a reputed diuretic and stimulating expectorant, especially applicable to chest diseases and rheumatism. Besides a trace of volatile oil and the constituents common to plants, senega root contains from 2 to 3·5 p.c. of *senegin* or *polygalic acid*, a compound which is nearly related to, if not identical with, saponin, as it occurs in soapwort and other plants. See Gehlen (B. J. 1804, 112), Dulong (J. Ph. 13, 567), Trommsdorff (N. J. T. 24, 2, 28), Quevenne (B. J. 17, 309; 18, 394), Bolley (A. 90, 211), Procter (C. N. 1861, 40), Christophsohn (J. 1875, 831), Kobert (Arch. Path. Pharmak. 23, 233). Senegin has the formula $C_{32}H_{52}O_{17}$ (Funaro, G. 19, 21). To obtain it the root is exhausted with a mixture of two-thirds alcohol and one-third water, and the liquid, after concentration, is washed by shaking with ether. The syrup thus freed from fixed oil and other substances is precipitated by a mixture of ether (1 part) and alcohol (3 parts), and the crude senegin which falls is finally purified by solution in water, and reprecipitation by ether-alcohol (Procter). By the action of dilute acids it breaks up into *sugar* and *senegein* thus: $C_{32}H_{52}O_{17} + 2H_2O = C_{20}H_{32}O_7 + 2C_6H_{12}O_6$ (Funaro) (*v.* Glucosides). According to Kobert, senega contains a second glucoside having acid properties, for which he adopts the name *polygalic acid.*

The 'Virginic acid' of Quevenne and the 'isolusin' of Peschier have not been found by subsequent inquirers. Langbeck (Ph. Z. 1881, 260) first detected methyl salicylate in old specimens of senega, which he supposed to be a product of decomposition of the root. Reuter (Ar. Ph. [3] 27, 309) has, however, shown that the *volatile oil* of senega consists of a mixture of methyl salicylate and valerianate.

For adulteration of commercial senega root, see Maisch (Ph. [3] 20, 547; 21, 46). A. S.

SENEGAL GUM *v.* Gums.

SENEGIN, SENEKA, SNAKE ROOT, *v.* Senega root.

SENNA LEAVES. *Folia Sennæ.* (*Feuilles de Séné*, Fr.; *Sennesblätter*, Ger.)

This well-known purgative was introduced into European medicine by the Arabian physicians. As it now occurs in commerce, the drug consists of the leaves of *Cassia acutifolia* (Delile) and *Cassia angustifolia* (Vahl). The former species inhabits Nubia and Kordofan, and produces what is known as Alexandrian senna. The latter is cultivated in southern India, and is the source of Indian or Tinnevelly senna (*cf.* Bentl. a. T. 90; Royle, Ill. Bot. Himal., 37).

Senna has frequently been the subject of chemical investigation. The earlier work of Braconnot (J. de Chim. Méd. 1, 284), Lagrange (A. Ch. 24, 3), and Lassaigne and Fenuelle (A. Ch. [2] 16, 16) showed that it contains a peculiar extractive, *cathartin*, together with a *yellow colouring matter*, *volatile* and *fixed oil*, and other constituents common to plants. Bley and Diesel (Ar. Ph. [2] 55, 257) isolated a yellow resin, *chryoretin*; but the investigations of Martius (Monographie der Sennesblätter, Leipzig, 1857), Batka (J. 1864, 555) and Bourgoin (J. Ph. [4] 5, 25; 12, 305) proved that this substance, the yellow colouring matter of senna, is nearly related to *chrysophanic acid.* Bourgoin isolated besides, a dextrorotatory *sugar*, and a substance which he termed *chrysophanin.* Two other compounds were obtained by Ludwig (Ar. Ph. [2] 119, 50) from an alcoholic extract of the leaves by treatment with charcoal—the one, *sennacrol*, soluble, and the other, *sennepicrin*, insoluble in ether (*v.* Gm. 18, 240).

How far these substances really represent the definite constituents of senna must be left for future investigation to determine, but in the meantime a distinct advance has been made by Dragendorff and Kubly (P. Z. 1866, 4, 429; 4, 465) and independently by T. B. Groves (Ph. 1869, 10, 196). These observers have brought to light a colloidal glucoside, *cathartic acid*, which, in combination with calcium or magnesium, exists in senna, and to which the purgative action of the drug is due. At all events, this property in its entirety is possessed by ammonium cathartate as prepared by Groves.

The cathartates which exist in senna are insoluble in alcohol but soluble in water or mixtures of water and alcohol. To extract them Dragendorff and Kubly treat a concentrated aqueous extract with an equal bulk of alcohol, which removes, by precipitation, mucilage and certain inactive salts. An excess of alcohol is then added, when the cathartates are thrown down. The precipitate, after washing with alcohol, is purified by solution in water and a repetition of the above process. To obtain the free acid, a concentrated solution of the salts in water is decomposed by hydrochloric acid, when the acid is precipitated. Cathartic acid is amorphous, of a brown to black colour, and though itself insoluble in water, forms soluble salts with metals of the alkalis and alkaline earths. Analysis led to the formula $C_{180}H_{96}O_{82}N_2S$ showing without doubt that the product was impure. According to Stockmann (Ph. [3] 15, 749) the acid when pure contains no nitrogen or sulphur. By the action of dilute acids cathartic acid breaks up into *glucose* and a new compound, *cathartogenic acid*, a yellowish-brown powder insoluble in water and ether.

From the alcoholic solution after removal of the cathartate the same investigators isolated *cathartomannite* $C_{42}H_{44}O_{19}$ (?), which was further studied by Stockman and by Seidel (Am. J. Pharm. 1885, 557), and which is no doubt the dextrorotatory sugar of Bourgoin; *chrysophan* or *chrysophanic acid*, as previously described by Bley and Diesel and others; and perhaps Ludwig's *sennepicrin*.

Senna pods appear to contain a greater proportion of cathartic acid than the leaves, and are said to be unattended by the pain in the intestines and nausea which generally accompany the administration of the leaves. See Macfarlane (Lancet, 1889, 164) and Salmon (Ph. [3] 20, 281). A. S.

SENNAAR GUM *v.* GUMS.

SENNACROL *v.* SENNA LEAVES.

SENNAPICRIN *v.* SENNA LEAVES.

SEPIA. A dark-brown pigment prepared from a black juice secreted by certain glands of the cuttle-fish (*Sepia officinalis*, *Sepia Loligo*, &c.) and ejected by the animal to darken the water when it is pursued. One part of the juice is capable of making 1,000 parts of water nearly opaque. The juice, when dried, yields a black mass, which, according to Prout, consists of 78 per cent. black pigment or melanin, 10·40 calcium carbonate, 7·00 magnesium carbonate, 2·16 alkaline sulphates and chlorides, and 0·84 mucus. The black pigment may be isolated by boiling the black mass successively with water, hydrochloric acid, and dilute solution of ammonium carbonate. It is a black, inodorous, and tasteless substance, quite insoluble in water, alcohol, and ether, but remaining suspended in water for a very long time; its deposition may, however, be accelerated by addition of acids or sal-ammoniac. It dissolves in warm caustic potash solution, forming a dark-brown solution, from which it is precipitated by sulphuric and hydrochloric acids, but not by nitric acid. It dissolves also in ammonia, but not in alkaline carbonates.

The pigment is prepared by saturating the dried native sepia with a little caustic lye, then adding more lye, boiling the liquid for half an hour, filtering, precipitating with an acid, washing the precipitate, and drying it at a gentle heat. It is of a dark-brown colour and fine grain.

Os sepiæ, *Meerschaum*, or *White fish-bone*, is the calcareous shell lying within the back of the cuttle-fish. It consists of two layers; the upper thin, but very compact, while the lower is thicker, but porous. The upper layer contains, according to John, 80 per cent. calcium carbonate with traces of phosphate, 9 gelatinous substance, insoluble in water and in cold lime-water, 4 water, and traces of magnesia. The lower layer contains 85 calcium carbonate with traces of potash, 4 gelatinous matter, and 4 water, with traces of magnesia. Forchhammer found in *Os sepiæ* 0·10 per cent. magnesium carbonate.

Os sepiæ is used as tooth-powder, for polishing, and for modelling for fine gold articles; it was formerly used as an internal remedy in cases of goitre (Watts' Dict. 5, 234, 1869 ed.).

SEPTARIA (from *septum*, 'a division'), called anciently *ludus Helmontii* (the *quoits* of Van Helmont, from their form), are argillo-calcareous concretions intersected by veins of calcspar, which, when calcined and ground to powder, form an excellent hydraulic cement.

From the regular arrangement of cracks in septaria, which generally assume pentagonal forms resembling in appearance the divisions in the shell of a tortoise, they have received the common name of 'turtle stones' or 'fossil tortoises.' The turtle stones found in the Oxford clay at Weymouth, when cut into slabs and polished, form very handsome tables. The number of veins of calcspar, upon which their beauty depends, renders these turtle stones unfit for forming an hydraulic cement, in consequence of their furnishing too great a quantity of lime when calcined. Septaria fit for furnishing cement are dredged in large quantities in Chichester harbour and off the coast of Hampshire, and are also procured from Harwich, Sheppey, and several other places. A stratum of septarian stone, forming the Broad Bench on the coast of Dorsetshire, affords an excellent cement and is largely quarried (Ure). (*V.* also CEMENTS.)

SERPENTINE. A rock much used as a decorative stone, and often popularly called a 'marble.' It has about the same hardness and density as ordinary marble, but is usually tougher and does not possess a crystalline texture. Essentially, it is a hydrous magnesium silicate, with more or less iron. An analysis of Lizard serpentine (sp.gr. 2·59) by J. A. Phillips, gave—silica, 38·86; alumina, 2·95; ferric oxide, 1·86; ferrous oxide, 5·04; nickel oxide, 0·28; chromic oxide, 0·08; magnesia, 34·61; potash, 0·33; soda, 0·77; water, 15·52 (P. M. [3] 51, 1871, 101). Rammelsberg regards the pure mineral as having the formula $H_2Mg_3Si_2O_8 + H_2O$ (Zeit. deutsch. geol. Gesel. 21, 1869, 98).

Serpentine, as a rock, usually exhibits dark shades of green and red, variously clouded and blotched, like the skin of a serpent, whence its common name, as also the term *ophite* (ὄφις, a serpent), by which it is sometimes known. The rock may be veined with steatite, or rendered more or less porphyritic by inclosed crystals of bastite or bronzite, or may contain garnets, usually altered to kelyphite or chlorite, as may be well seen in the pyrope-bearing serpentine of Zöblitz, in Saxony. The beauty and variety of its colours have led to the extensive use of serpentine for vases and other ornamental objects. It is also employed for mantel-pieces and architectural columns, but the rock is usually so broken up by joints that it is difficult to procure slabs of large size. While valuable for indoor decoration, it is apt to yield on exposure to the atmosphere, gradually losing lustre and presenting an eroded surface. From its refractory behaviour on exposure to heat, it is sometimes employed in the construction of ovens. It has also been used as a source of certain magnesium salts, such as the sulphate.

Serpentine has been extensively worked in the Lizard district in Cornwall, but not elsewhere in Britain, though it occurs in Anglesea, in Ayrshire, and in Banffshire. The British serpentines have been specially studied by Prof. Bonney; an excellent account will be found in Teall's 'British Petrography,' 1888, 104. On the Continent, serpentine has been worked for centuries at Zöblitz and elsewhere in Saxony. It is also wrought in the Vosges and in the departments of the Hautes Alpes, Lot, and Aveyron in France; while in Italy the most famous locality is at Prato in Tuscany, which yields a dark-green variety known as *verde di Prato*, resembling when polished an antique bronze, and hence largely used for statues &c.

A fine translucent variety, known as *noble* or *precious serpentine*, of oil-green or yellowish-green tint, is worked at Snarum, in Norway. Pseudomorphs of serpentine after olivine, occurring at this locality and retaining in some cases a nucleus of the original mineral, first suggested that serpentine might be an alteration-product of olivine. It has been shown by Sandberger, Tschermak, Bonney, Roth, and others that most serpentines have been derived from peridotites, or rocks rich in olivine, though other minerals, such as hornblendes and pyroxenes, may also be converted into serpentine. The microscopic structure of serpentine frequently reveals its origin; thus a hornblende-serpentine shows the characteristic cleavage of the original mineral in lozenge-shaped lattice work, while an augite-serpentine has frequently a rudely rectangular network of cleavages, and an olivine-serpentine an irregular mesh-structure corresponding with the fissures in the primitive mineral. J. D. Dana has shown that serpentine may be produced from a great range of minerals, as testified by the pseudomorphs from the Tilly Foster mine, Putnam Co., New York (Am. S. [3] 8, 1871, 371). F. E. Becker has traced the origin of certain Californian serpentines to the alteration of felspar and other minerals (U. S. Geol. Sur., Mon. 13, 1888). On the conversion of dolomite into serpentine *v.* Dobbie and Henderson, Proc. R. S. Ed., 11, 1882, 606. T. Sterry Hunt has argued in favour of the origin of serpentine by the reaction of soluble silicates on the magnesium salts of natural waters (Trans. R. S. Canada, 1 [4] 1883, 165). For American serpentines *v.* Merrill in Smithsonian Rep. for 1886, part 2, 361.

Several varieties of serpentine have received distinctive names. *Picrolite* is the term applied to the mineral when presenting a columnar or fibrous structure, while an asbestiform variety with silky fibres is known as *chrysotile.* Much of the mineral used in the arts under the name of asbestos, or amianthus, occurs in veins running through serpentine, especially in Canada, and is really chrysotile (*v.* R. H. Jones, Asbestos, London, 1890). Serpentine with a lamellar structure is termed *marmolite*, and a shaly variety of dark-green colour from the Antigorio valley in Piedmont is known as *antigorite. Williamsonite* is a translucent apple-green serpentine, found in limited quantity at a chromite mine in Chester Co., Pa., and cut as an ornamental stone. An exceptionally hard serpentine, termed *Bowenite*, has been mistaken for jade, and MacMahon has shown that the so-called jade of Afghanistan is of this character. (Min. Mag., 9, 1890, 187).

Serpentine frequently carries chrome iron-ore; and crystals of chromite and picotite are common microscopic inclosures in the rock. Native copper also occurs in serpentine, and large masses upwards of a ton in weight were obtained many years ago from fissures in serpentine at the Trenance mine, near Mullion, in Cornwall.

It is not uncommon for serpentine to be intimately associated with limestone or dolomite, forming a rock known as *ophicalcite*, *ophiolite*, or *serpentinous marble.* The composite rock, being variegated with green and white colours, is prized as an ornamental material, but on exposure to atmospheric influences a differential action is set up, and the surface becomes unequally eroded. The famous *Verd antique* is a brecciated ophiolite (*v.* Marble).

F. W. R.

SERUM ALBUMIN *v.* Albuminoids.

SERUM GLOBULIN *v.* Albuminoids.

SESAME OIL. *Gingelly* or *Gingili oil*; *teel*, *til*, *beni* or *benné oil.* This important oil is principally prepared from the seeds of the *Sesamum indicum* (India), and the *Sesamum orientale* (Levant), a small quantity being also obtained from the *Bignonia tomentosa* of Japan.

The composition of the two first is as follows:

	Levant	India
Oil	55·63	50·84
Organic substances other than oil	30·95	35·25
Ash	7·52	6·85
Water	3·90	7·06
	100·00	100·00

The seeds from the Levant are brownish or black, and are preferred to the yellowish seeds from India, both on account of the extra quantity obtained and of the finer quality of the product.

The oil is usually expressed in three operations. The first pressure gives (in the case of the Levant seeds treated in Marseilles) 30 p.c. of the finest oil. The second pressure, which is performed after the mass has been softened with cold water, gives a further 10 p.c., also of fine quality, and the third pressure, after treatment of the residue with steam or hot water, gives 10 p.c. of oil of 'ordinary' quality.

Sesamé oil is of a fine golden-yellow colour, almost odourless, of a mild flavour, and having but little tendency to become rancid. It resembles cotton-seed oil, and is used on an immense scale to adulterate or replace olive oil. It is also used as an illuminant and for soap-making, and is said to be the source of the soot employed in making Indian and Chinese inks.

Sesamé oil is said to be frequently adulterated with ground-nut oil.

It contains about 76 p.c. of olein in addition to myristin, palmitin, and stearin, and a small quantity of a resinous (?) substance soluble in alcohol or glacial acetic acid.

The specific gravity of sesamé oil at 15° to 15·5°C. is 0·921 to 0·922. The oil expressed from the seeds congeals at about −5°C.; that removed by solvents congeals at about +5°C.

German sesamé oil or camelina oil, is prepared from the seeds of *Camelina sativa* (gold of pleasure) and of *Camelina dentata*. Its specific gravity at 15°C. is 0·925 to 0·926, and its congealing point is −15°C.

The seeds give 10–20 p.c. of oil by cold pressure, a total of 23–25 p.c. when hot pressed, and 28 p.c. by extraction. Their average composition is:—

Oil	29·50
Organic substances other than oil	56·58
Ash	6·42
Water	7·50
	100·00

The oil consists of glycerides of oleic and palmitic acids, and also contains erucic acid and an acid allied to linoleic acid. It is principally employed as a lamp oil and for soap-making.

SHALE OIL *v.* PARAFFIN OIL.

SHANGHAI OIL. A variety of colza oil *v.* OILS AND FATS.

SHEA BUTTER. A vegetable fat made in West Africa by boiling the kernels of the nuts of *Bassia Parkii*. It is a greenish-white substance, melting at 43°, and readily soluble in alcohol and ether. Consists mainly of a glyceride of oleic and stearic acids free from palmitic acid.

SHELLAC *v. Lac resins*, art. RESINS.

SHODDY. The term 'Shoddy' is intended to apply to all artificially-recovered wool, although there is no exact English equivalent to the German 'kunstwolle,' which includes all the recovered material from mungo, shoddy, and 'extract,' or wool from mixed goods. The industry was introduced from England into Germany by Gustav Köber in 1851 at Cologne, and, after some early struggles, flourished at Mannheim, spreading thence to all parts. To Köber is due the method of separating woollen from vegetable fibres by treatment with sulphuric acid. In such a manufacture the collection, sorting, and cleaning of the raw material are of much importance, but present little technical interest. The separation of vegetable fibres calls, however, for a more detailed account. Two processes are in use, the wet and the dry; in the former the raw material is soaked in sulphuric acid of 4°–7°Bé. for 12 hours, the greater part of the acid removed from it in a centrifugal machine and dried at 40°–50°C., after which it is carbonised at 90°–95°C. In the latter it is treated with gaseous hydrochloric acid. In either case the carbonised vegetable fibre is beaten out. The recovered wool felts badly.

It is estimated that at least 100–150 million kilos. of recovered wool are produced yearly in Europe. Ten years ago only 34 p.c. of the cloth made in England was prepared from pure new wool and 9 p.c. of woven fabrics, and these figures are considerably too high for the present state of the trade (J. Harzfeld, Chem. Zeit. 14, 903–904; S. C. I. 9, 935).

SIEMENS STEEL *v.* IRON.

SIENNA *v.* PIGMENTS.

SILEX, SILICA *v.* SILICON.

SILICATE COLOURS *v.* PAINTS AND PIGMENTS.

SILICATE PAINTS *v.* PAINTS AND PIGMENTS.

SILICEOUS CEMENTS *v.* CEMENTS.

SILICON. Symbol Si. At. wt. = 28·33 (Thorpe and Young, C. J. 1887 [Trans.] 578). Silicon never occurs in nature in the free state, but abundantly as silica and metallic silicates. It is obtained by reducing the chloride or fluoride, and is known in three modifications—amorphous, graphitoidal, and crystalline.

1. As amorphous silicon, it was first obtained by Berzelius (1823), by heating dry potassium or sodium silicofluoride with about an equal weight of potassium or sodium respectively. The metallic fluoride formed is well washed with cold and then with hot water.

2. It may also be prepared by passing the vapour of silicon chloride over potassium or sodium heated in porcelain trays in a glass tube lined with mica.

3. By electrolysis of a fused mixture of potassium fluoride and silicofluoride.

Thus obtained it is a dull-red powder, insoluble in water, and in nitric and sulphuric acids, but readily soluble in hydrofluoric acid and in warm potash.

It is fusible in a non-oxidising atmosphere at a temperature between the melting-points of steel and cast-iron, but burns brilliantly in presence of air and oxygen, silica being formed. It is a non-conductor of electricity, and soils the fingers.

It is deposited by the electrolysis of a fused mixture of 300 grains of 97·1 p.c. potassium carbonate and 442 grains of potassium fluosilicate (Gore, C. N. 50, 113).

Graphitoidal silicon is obtained by heating strongly amorphous silicon in a platinum crucible (Berzelius).

Shining metallic scales resembling graphite were also obtained by Deville on treating the aluminium contaminated with silicon, which he obtained by electrolysing the sodium aluminium chloride with hydrochloric acid, which dissolves out the aluminium.

When aluminium is mixed with from 20 to 40 times its weight of potassium fluosilicate, and the mixture heated to the melting-point of silver in a Hessian crucible, a metallic button is obtained which yields graphitoidal silicon on successive treatment with hydrochloric and hydrofluoric acids, in hexagonal tables with curved edges (Wöhler, C. R. 42, 48).

It is also obtained by fusing 1 part of aluminium with 5 parts of glass free from lead, and 10 parts of powdered cryolite, the mass being treated successively with hydrochloric and hydrofluoric acids. Density = 2·49. Is not altered in oxygen at a white heat, but burns brilliantly when heated to redness with potassium carbonate, silica being formed. With nitrate and chlorate of potassium it fuses without alteration at a red heat, but at a white heat it burns brilliantly, especially when a little potassium carbonate is present. It is unattacked by acids, except by a mixture of nitric and hydrofluoric acids. It is soluble in strong potash or soda, and burns in chlorine when heated to redness, forming silicon chloride. It combines with fluorine at ordinary temperatures forming silicon tetrafluoride.

Crystalline or adamantine silicon was obtained by Deville on heating silicon, in a platinum crucible lined with lime, to a temperature between the melting-points of steel and cast-iron. It is thus obtained in dark steely grey globules, sometimes yielding double six-sided pyramids (Deville, A. Ch. [3] 49, 68)

When vapour of silicon fluoride is passed over aluminium fused in an atmosphere of hydrogen, a portion of the aluminium volatilises as chloride, and the remainder becomes saturated with silicon. At the point of saturation the excess of silicon is separated in large beautiful needles of dark iron-grey colour, reddish by reflected light, and iridescent. The form is derived from a rhombic octahedron, and the crystals often exhibit curved faces. They are capable of cutting glass.

Another and easier method is to heat at a red heat in an earthen crucible a mixture of 3 parts potassium fluosilicate, 1 part of sodium in small pieces, and 4 parts of granulated zinc. The heat must not be sufficiently high to volatilise the zinc. The mass of zinc thus obtained contains the silicon in the form of long needles. The zinc is removed by fusing, and then by hydrochloric, and, lastly, by boiling nitric, acid (Deville and Caron, A. Ch. [3] 63, 26; *ibid.* [3] 67, 441; Robins, C. N. 5, 102). It appears that silicon is retained by aluminium up to 1300°C., but is given up at a temperature approaching the melting-point of aluminium (Hautefeuille and Perry, C. R. 100, 1220). For the estimation of silicon in iron and steel, *v.* Marston, C. N. 29, 107; Troost and Hautefeuille, Ann. M. 1874, 4, 1; Drown, C. N. 40, 40; Haswell, D. P. J. 237, 314; Drown and Shimer, C. N. 42, 299; F. Watts, C. N. 45, 279; D. P. J. 248, 213; Turner, C. J. Trans. 1884, 260; *ibid.* 1885, 577, 902; *ibid.* 1887, 129; Jordan and Turner, C. J. 1886, 130; *ibid.* 1886, 215; Strick, D. P. J. 262, 384; Morgan, C. N. 56, 82; Gautier, C. R. 103, 1137).

Silica. *Silicic acid, silex*, SiO_2.

The only known oxide of silicon occurs abundantly in nature, pure, or nearly so, in quartz, flint, chalcedony, hornstone, jasper, opal; sometimes crystalline, sometimes amorphous. It enters largely into the constitution of sandstones, felspar, and many other rocks.

It may be artificially prepared:

1. By burning silicon in air or oxygen.

2. By the action of water upon silicon fluoride a gelatinous hydrate is obtained which yields pure anhydrous silica on ignition as a fine white powder.

3. By decomposing alkaline silicates. The silicate, in fine powder, is added in small portions at a time to fused sodium potassium carbonate; the mass is further heated, allowed to cool, and treated with dilute hydrochloric acid. On evaporating the solution thus obtained, the silica separates out as a gelatinous hydrate, from which anhydrous silica may be prepared as above by ignition. It is further digested with sulphuric acid to remove titanic oxide, freed from the acid by decantation, and again dried and ignited.

It occurs in nature both crystalline and amorphous, the crystalline variety having a sp.gr. between 2·5–2·8, the amorphous from 1·9–2·3, the crystalline being also the harder.

It is infusible except at very high temperatures, but melts to a transparent glass in the oxyhydrogen flame, or in that of a burner fed with oxygen, and may be drawn out into long threads.

It is non-volatile, but is said to volatilise when heated very strongly in a current of steam (Gmelin, Handb. 3, 355).

It decomposes fused sodium carbonate and melts to a transparent glass. It is insoluble in fused microcosmic salt. It is insoluble in water and all acids except *hydrofluoric acid*, which decomposes it into water and silicon fluoride. The gelatinous hydrate obtained by decomposing silicon fluoride with water dissolves, however, in large quantities of water.

Silica dissolves readily, as a rule, in caustic alkalis, forming solutions of the alkaline silicate (water-glass). Hyalite dissolves more slowly than the other varieties, and quartz requires boiling or an increased pressure.

Amorphous silica in fine powder and gelatinous silica dissolve partially in alkaline carbonates, the silica being deposited on cooling in the form of a jelly containing some of the alkali. It is on this account that most spring and river waters contain traces of silica.

Silica is decomposed at a red heat by potassium into potassium silicide and silicate; by carbon in presence of iron, copper, or silver, at a white heat, carbon monoxide and a metallic silicide being formed.

Silicic acids. Four silicic acids are usually stated to exist, viz.:

Orthosilicic acid, H_4SiO_4
Metasilicic acid, H_2SiO_3
Polysilicic acid, $H_4Si_3O_8$
Disilicic acid, $H_2Si_2O_5$.

Polysilicic acid may be regarded as composed of metasilicic and disilicic acids: $H_2S_2O_5 + H_2SiO_3 = H_4Si_3O_8$ (Groth).

On the other hand, orthosilicic acid and polysilicic acids may combine together to form metasilicic acid: $H_4SiO_4 + H_4Si_3O_8 = 4H_2SiO_3$; and disilicic acid may be regarded as polysilicic acid from which orthosilicic acid has been abstracted: $3H_4Si_3O_8 - H_4SiO_4 = 4H_2Si_2O_5$ (Becker, Am. S. 38, 154).

Metasilicic acid, $H_2O.SiO_2$ or H_2SiO_3, is obtained as a gelatinous precipitate when an acid is added to the solution of an alkaline silicate.

If a dilute solution of the alkaline silicate be poured into a large excess of hydrochloric acid, the silica remains in solution, but may be precipitated by neutralising the acid.

A solution of hydrate of silica (soluble silica) may be obtained from the above by dialysing the solution in hydrochloric acid by means of parchment-paper. If a stratum $\frac{2}{5}$ of an inch in depth be subjected to dialysis for four or five days, the hydrochloric acid and chlorides gradually but completely diffuse into the water.

The solution in the dialyser contains 5 p.c. silica, and it may be concentrated by evaporation to 18 p.c. The solution is tasteless, limpid, and colourless, with a slightly acid reaction. The solution is difficult to preserve, as it readily coagulates. Hydrochloric acid and small quantities of potash or soda retard the coagulation.

Sulphuric, nitric, and acetic acids are without action upon it; but carbonic acid, and a trace of any soluble alkaline or earthy carbonate except ammonia and its salts, solutions of gelatine, alumina, and ferric oxides coagulate it; alcohol, sugar, gum, and caramel do not.

The solution evaporated at 15° *in vacuo* leaves the silica as a transparent, glassy, lustrous hydrate containing 21·99 p.c. water (Graham, T. 1861, 204).

The coagulation of colloid silica is accompanied by an evolution of heat equal to 11·8 cals. (Wiedemann and Lüdeking, A. Ch. [2] 25, 145).

The following hydrates were obtained by Wöhler:—

1. **Leucone** $Si_3H_4O_5$ may be regarded as the hydrate of a monoxide, $3SiO.2H_2O$, produced by the action of water on *chryseone* under the influence of light.

It is best prepared by heating crystalline silicon to redness in chlorine, and passing the resulting compound into water. It is then washed, pressed, and dried over sulphuric acid. It is a snow-white, amorphous, bulky substance, lighter than water, permanent at ordinary temperatures, not being altered at 300°; more strongly heated it gives off hydrogen. Heated in the air it glows with a bright light, depositing silica. It is slightly soluble in water, but the solution gradually decomposes. It is readily soluble in caustic alkalis and carbonates, with evolution of hydrogen and formation of silicate. When freshly prepared it is a powerful reducing agent (Wöhler and Buff, A. 104, 101; Wöhler, A. 127, 257).

2. **Chryseone or silicone** $Si_4H_4O_3$ (?) is prepared by digesting calcium silicide in fine powder with fuming hydrochloric acid in a closed vessel in a dark place for several hours, till hydrogen is no longer evolved. The liquid is then largely diluted with water and filtered. The residue is washed and dried over sulphuric acid *in vacuo* in the dark.

Chryseone forms orange-coloured laminæ, insoluble in water, silicon tetrachloride, phosphorus trichloride, carbon bisulphide, and alcohol. It darkens on heating, and at a higher tempertaure burns with a slight detonation and scintillation. When mixed with the next compound (γ) it detonates on heating in a tube, giving off spontaneously-inflammable silicic hydride. Heated to 100° by itself or with water it becomes paler.

It remains unaltered in the dark, in diffused daylight it becomes paler, and in direct sunshine, even under water, is converted into leucone with evolution of hydrogen.

It is not attacked by chlorine or strong acids, but is soluble with evolution of heat in hydrofluoric acid. It is decomposed by alkalis, and in the presence of an alkali reduces many metallic salts.

The results of analysis correspond partly with the formula $Si_4H_4O_3$ and partly with $Si_6H_6O_4$; according to the first its formation may be represented thus:—

$$2CaSi_2 + 4HCl + 3H_2O = Si_4H_4O_3 + 2CaCl_2 + 3H_2.$$

It may be regarded as the hydrate of a tetrasilicic oxide, $Si_4O.2H_2O$.

γ. $Si_4H_8O_5 = Si_4O.4H_2O$. This compound, which differs from chryseone by two molecules of water, is produced by the action of cold dilute hydrochloric acid upon calcium silicide. It forms colourless transparent nacreous laminæ, which take fire spontaneously in air and burn, leaving brown silica (Wöhler, A. 127, 257; J. 1863, 205).

Hydrated silica may also be prepared by pouring dilute oxalic acid upon a solution of an alkaline silicate in an inclined vessel. A layer of transparent silica forms at the surface of contact after several months. The silica thus obtained possesses the properties of hydrophane. It is transparent, very hard, being capable of scratching glass, has much hygrometric water, of which it gives off all but 9–13 p.c. at 30–35°, becoming opaline. It is singly refractive, and possesses a density = 2·03–2·07 (Monier, C. R. 86, 1318).

The gelatinous silica formed by pouring dilute solution of water-glass into hydrochloric acid may be completely washed with water without loss of coherence. It is thus obtained perfectly pure as a translucent gelatinous mass, which dries up in the air to a substance resembling hyalite, splitting up into large and small particles. Hygroscopic, sp.gr. immediately after ignition = 2·323, which is that of tridymite.

The silica thus obtained has been used as a membrane in dialysis (Ullik, B. 11, 2124). Le Chatelier finds that on dialysing a solution of a silicate with an alkaline solution of alumina a precipitate is formed, consisting of silica or alumina, according to which was in excess (Le Chatelier, C. R. 78, 1046).

Soluble silica is readily obtainable by boiling 8 grms. methyl silicate with 200 grms. water with a reversed condenser, and evaporating the liquid to $\frac{3}{4}$ to expel the methyl alcohol. The solution thus obtained contains 2·26 p.c. of anhydrous silica (Grimaux, C. R. 98, 1434).

For hydraulic silica and its functions in cements *v.* Laudrin, C. R. 96, 156 and 379. Hydraulic silica is the name given by Laudrin to silica precipitated from potassium silicate, well washed, and ignited at a dull-red heat. This, when mixed with lime, sets under water.

For the action of silica upon alkaline haloid salts *v.* Gorgeu, C. R. 102, 1164.

Artificial quartz and tridymite have been prepared by Chroustchoff, J. M. 1887, 205; C. R. 104, 602).

Silica gradually absorbs lime from lime-water, forming ($3SiO_2,4CaO$), the maximum absorption being between 36 and 38 parts lime for one equivalent of SiO_2. The absorption is most rapid with soluble silica. Silica from hydrofluosilicic acid absorbs lime more slowly than the hydraulic, gelatinous, or soluble varieties (Laudrin, C. R. 96, 841).

A series of experiments performed by Kreuzhage and Wolff show that silica acts like phosphoric anhydride in greatly assisting the assimilation of other plant foods; and the authors suggest the possibility of supplanting phosphoric by silicic acid in artificial manures (Kreuzhage and Wolff, L. V. 30, 161, 198).

The deprivation of silica in the cultivation of maize produces no degeneration in the plants, which can be cultivated through several generations under similar conditions (V. Jodin, C. R. 97, 344).

Hydrated silica dissolves readily in orthophosphoric acid; the solution deposits crystals in forms varying with the temperature at which the deposition takes place (Hautefeuille, C. R. 99, 789).

When a concentrated solution of phosphoric acid, containing about one-fourth of the quantity of silica necessary to saturate it, is heated to 125° for a week, a hydrated silicon phosphate of the composition $SiO_2,P_2O_5.4H_2O$ is obtained (Hautefeuille and Margottet, C. R. 104, 56).

For compounds of silica with metaphosphoric acid *v.* Hautefeuille and Margottet, C. R. 96, 1052.

The following series of hydrates has been obtained by Merz: SiO_2,H_2O, Graham's monohydrate; $2SiO_2,H_2O$, by repeated washings and drying for six weeks at 20–25°C.; $3SiO_2.H_2O$, by drying above at 60°, or after prolonged desiccation over sulphuric acid; $4SiO_2.H_2O$ (very unstable), at 80–100°; $8SiO_2.H_2O$, dried at 250°–270° (Merz, J. pr. 99, 177; *v.* also Gottlieb, J. pr. [2] 6, 185).

The hydrate obtained by the action of moist air on silicon tetrachloride has the composition $9SiO_2.4H_2O$, according to Langlois (J. 1858, 140).

Ammonia dissolves small quantities of amorphous silica, both gelatinous and ignited, even pulverised quartz being dissolved.

100 parts of aqueous ammonia, containing 10 p.c. NH_3, dissolve

Crystal. silica	0·017 parts
Amorphous, ignited	0·38 ,,
,, hydrate	0·21 ,,
,, gelatinous	0·71 ,,

(Wittstein, J. 1866, 192); *v.* also Pribram (Fr. 6, 119), Souchay (Fr. 1872, 182).

Silicon fluoride SiF_4 is formed by the action of hydrofluoric acid upon silica or a silicate. It is prepared by heating a mixture of fluorspar and sand or glass in fine powder, with strong sulphuric acid, the gas being collected over mercury in dry glass jars. It is a colourless gas, possessing a suffocating odour. It neither burns nor supports combustion, and fumes strongly in the air. Under strong pressure it liquefies (Faraday), and solidifies to a white amorphous mass at −140° (Natterer), or at −102°, according to Olszewski (M. 5, 127).

SiF_4 is readily absorbed in large quantities by water being at the same time decomposed into silica and hydrofluosilicic acid, according to the equation $3SiF_4 + 2H_2O = 2(2HF,SiF_4) + SiO_2$, the decomposition of an equivalent of water evolving 22·34 cals. according to Hammerl (C. R. 90, 312), 25·8 cals. according to Guntz (A. Ch. [6] 3, 1–66).

Aqueous alkalis and alkaline earths decompose it, precipitating part of the silica and forming a fluosilicate of the metal, as is the case with potash, or precipitating the whole of the silica and forming a metallic fluoride, as is the case with soda.

Many *anhydrous metallic oxides* absorb silicon fluoride, becoming hot, and sometimes taking fire.

Potassium and *sodium* do not act until melted, when they blacken and burn with a dark-red flame, yielding a dark-brown brittle mass (Gay-Lussac and Thénard).

Silicon fluoride combines with twice its volume of ammonia-gas, forming a volatile crystalline compound $(2NH_3)SiF_4$, which is decomposed by water in the following manner:

$$2((NH_3)_2SiF_4) + 2H_2O$$
$$= 2NH_4F + (NH_4)_2SiF_6 + SiO_2$$

(J. Davy). It is absorbed by absolute alcohol forming fluosilicic alcohol, a mixture of tetrethylic silicate and hydrofluosilicic acid (Knop and Wolf, C. C. 1861, 82; J. 1861, 207).

Silicon subfluoride, probably a trifluoride, has been prepared as a white, very light powder, by passing the tetrafluoride over silicon heated nearly to the softening point of porcelain. With water it yields a hydrated oxide similar to that obtained from the trichloride (Troost and Hautefeuille, C. R. 73, 563).

Hydrofluosilicic acid. *Silicofluoric acid* H_2SiF_6 or $2HF.SiF_4$. An acid produced by the action of water on silicon tetrafluoride.

The apparatus employed for the preparation of SiF_4, as above, is connected with a perfectly dry tube dipping under mercury at the bottom of a glass jar. The jar is then filled with water, and heat applied to the mixture in the flask. The object of first passing the gas through mercury is to prevent the tube being stopped up by the deposition of silica. Each bubble of gas is decomposed as it comes in contact with the water, hydrofluosilicic acid being formed, which remains in solution, and silica, which forms a siliceous envelope round each bubble. It is separated from the acid solution by filtration.

An easier method of preparation is to dissolve silica in hydrofluoric acid.

Hydrofluosilicic acid in concentrated solution is a very sour, fuming liquid, which gradually evaporates at 40° without leaving any residue in platinum vessels.

It does not attack glass unless evaporated upon it.

The sp.gr. of an aqueous solution increases regularly with its strength, as shown below:

Per cent. of H_2SiF_6	Sp.gr. at 17·5°
0·5	1·004
1	1·008
1·5	1·012
2	1·0161
5	1·0407
10	1·0834

(Stolba, J. pr. 90, 193).

Metallic fluosilicates are obtained by the action of metallic oxides, hydrate or carbonate, upon the above acid.

Silicon hydride SiH_4. First obtained, mixed with hydrogen, by Wöhler and Buff (A. 102, 128; 103, 218; 104, 94; 107, 112; J. 1857, 166, and 1858, 142). When a wire or plate of aluminium containing silicon is connected with the positive pole of a Bunsen's battery of 8 or 12 cells and made to decompose a solution of sodium chloride, the aluminium dissolves as chloride, and the gas formed escapes in bubbles, which take fire as they escape into the air, burning with a white light and emitting white fumes, the hydrogen being obtained from a secondary decomposition of the water.

The gas is likewise prepared from a silicide of magnesium, obtained by heating a mixture of 40 parts of fused magnesium chloride, 35 parts dry sodium fluosilicate, and 10 fused sodium chloride with 20 parts of sodium in small fragments. The mass thus obtained contains, according to Wöhler, two silicides of magnesium, one of which yields silicon hydride on treatment with hydrochloric acid or sal-ammoniac, the other yielding only hydrogen and hydrated silica.

The gas as thus obtained by Wöhler and Buff is colourless, spontaneously inflammable, insoluble in de-aërated water, but decomposed over water containing air.

It is readily decomposed by chlorine, and by potash with increase of volume; not decomposed by dilute acids, nor by soda nor ammonia.

Forms precipitates of silicides of copper and silver from solutions of the metallic salts, and throws down metallic palladium, free from silicon, from chloride of palladium.

Is without action on lead acetate or platinum chloride.

May be obtained in the pure state by the decomposition of triethyl silicoformate by sodium. The action of sodium has not been explained: $4SiH(OC_2H_5)_3 = SiH_4 + 3Si(OC_2H_5)_4$. Thus obtained it is a colourless gas, agreeing in character with that described by Wöhler and Buff, but not spontaneously inflammable, except when gently heated under reduced pressure or when mixed with hydrogen.

A hot knife-blade is sufficient to inflame the bubbles of gas as they rise over mercury, and the mercury becomes sufficiently heated to set fire to the succeeding bubbles (Friedel and Ladenburg, Bl. [2] 7, 322). It is decomposed by potash: $SiH_4 + 2KHO + H_2O = K_2SiO_3 + 4H_2$.

Silicon hydride prepared from magnesium silicide forms a solid and liquid compound with bromine, the former crystallising in needles.

With iodine it forms $SiHI_3$ and SiI_4. It is also decomposed by the chlorides of sulphur, phosphorus, antimony, and tin (Mahu, Z. [2] 5, 730).

The heat of combustion of one equivalent of silicon hydride in oxygen is 324·3 cals., being less by 24·8 cals. than the heat of combustion of its constituents.

The union of silicon and hydrogen is accompanied by the disengagement of 24·8 cals. (Ogier, C. R. 88, 91).

At $-11°$C. it is liquefied under 50 atmospheres, its critical point being situated about 0°; at $-5°$C. it is liquefied under 70 atmos.; at $-1°$C. it is liquefied under 100 atmos.; at 0°C. is gaseous under from 150 to 200 atmos. (Ogier, C. R. 88, 236).

It is decomposed by the electric current, hydrogen being liberated and a yellow substance deposited, probably SiH_3. This ignites on percussion and burns when heated in air. Burns also in chlorine (Ogier, C. R. 89, 1068).

Silicon tetrachloride $SiCl_4$. Formed when silicon is heated in chlorine gas. Also prepared by heating finely-powdered silica made into a paste with oil and charcoal in a covered crucible, and igniting the charred mass in a porcelain tube through which a current of chlorine is passed. Or by heating a deflagrated mixture of silica and magnesium powder in chlorine gas.

The product is collected in a vessel surrounded by a freezing mixture.

It is a colourless, transparent liquid, sp.gr. $\frac{0}{4}$ 1·52408, and boiling at 58–58·3° (Thorpe, C. J. 1880, 237).

Silicon tetrachloride remains liquid at $-20°$C. (Serullas). It is decomposed by water into hydrochloric acid and silica, and by potassium when heated in the vapour, silicon being formed.

If fused potassium be added to the liquid, an explosion takes place.

When silicon tetrachloride is repeatedly passed over fused silicon in a porcelain tube heated to near the softening-point of porcelain, with exclusion of air, sub-chlorides of silicon are formed, their decomposition being prevented by having a central cooling-tube traversed by a stream of water at 60°. The sub-chlorides have higher boiling-points than the tetrachloride, and may be separated from each other by fractional distillation (Troost and Hautefeuille, C. R. 73, 563).

Silicon trichloride Si_2Cl_6. Obtained by gently heating a mixture of silicon triiodide with mercuric chloride, rectifying, and purifying by fractional distillation. It is a colourless, mobile liquid, distilling at 144–148°; solidifies in crystals at 1°. Fumes in air, and is decomposed by water. Vapour density at 239·4° = 9·7 (Friedel and Ladenburg, A. Ch. [5] 19, 390; Friedel, C. R. 73, 1011).

Strongly heated, it gives off a vapour, taking fire spontaneously in the air. It is slowly decomposed when heated in closed vessels, the decomposition being complete at 800°. It is decomposed by cold aqueous ammonia, and with water at 0° forms a hydrate of the composition $SiO_3.H_2O$, which reduces potassium permanganate rapidly, and chromic acid slowly, in the cold, but is without action on gold chloride or selenious acid (Troost and Hautefeuille, C. R. 73, 563).

Silicon dichloride Si_2Cl_4. A liquid found mixed with the above, especially when oxychlorides are present in its formation. It is decomposed by aqueous ammonia, and the hydrate formed by contact with water at 0° reduces not only permanganate and chromic acid, but also solutions of gold and selenious acid (Troost and Hautefeuille, *l.c.*).

Trichlorosilicic oxide $O\begin{cases}SiCl_3\\SiCl_3\end{cases}$ is obtained by passing the vapour of silicon tetrachloride through an exhausted porcelain tube containing fragments of felspar, heated to near the softening-point of felspar. On repassing the more volatile products several times a mixture of silicic chloride and trichlorosilicic oxide is obtained, volatilising at 70°. These are separated by fractionating the oxychloride passing over between 136° and 139°. The oxygen is derived from the felspar. The same compound is formed, together with phosphorus oxychloride, when silicic chloride is passed over strongly-heated phosphoric anhydride.

It is a colourless, fuming liquid. Vapour density =10·05. It is decomposed by water and alcohol. With the latter it forms disilicohexethylic ether, $O\begin{cases}Si(C_2H_5)_3\\Si(C_2H_5)_3\end{cases}$, which boils at 235–237°.

When 1 molecule of the oxychloride is heated with 3 molecules zinc-ethyl, triethylsilicic oxide is produced, $O^{Si(C_2H_5)_3}_{Si(C_2H_5)_3}$ (Friedel and Ladenburg, Bl. [2] 9, 358).

Several oxychlorides are produced by the action of the induction spark on a mixture of the tetrachloride, trichlorosilicic oxide, and oxygen, or by passing the trichlorosilicic oxide, together with oxygen, several times over fragments of porcelain heated in a glass tube.

The following have been separated by fractional distillation:

Empirical formulæ	B. P.	V. D. at 440°
Si_2OCl_7	—	—
Si_2OCl_6	136–139°	—
$Si_4O_3Cl_{10}$	152–154°	—
$Si_2O_2Cl_4$	198–202°	15·5
$Si_4O_5Cl_6$	About 300°	21·2
$Si_4O_6Cl_2$	Above 400°	—
Si_4O_7Cl	Nearly (4 ?) 40°	—

(Troost and Hautefeuille, C. R. 73, 563).

Silicon oxychloride is formed, together with dichloride, when a heated mixture of chlorine, with one-half to one-fifth of its volume of oxygen, is passed over crystalline silicon (Troost and Hautefeuille, Bl. [2] 35, 360).

A compound, called **silicohydric chloride**, $Si_3H_4Cl_{10}$, was prepared by Wöhler and Buff by passing hydrochloric acid gas over crystallised silicon heated to low redness, the product being condensed in a vessel kept at 0°.

It is a colourless, mobile liquid; sp.gr. =1·65; boiling-point, 42°. It fumes strongly in the air, and is decomposed by water with rise of temperature, hydrochloric acid and the corresponding hydrate, $Si_3H_4O_5$ (leucone), being formed. It is highly inflammable, burning with a greenish flame. Mixed with oxygen, the vapour explodes on the passage of an electric spark. It may be boiled over sodium without decomposition.

It is decomposed when passed through a red-hot tube (Wöhler and Buff, A. 104, 94).

Friedel and Ladenburg have shown that the above consists of a mixture of $SiCl_4$ and *silicic chloroform*, $SiHCl_3$, which may be separated by fractionating between 55° and 60°C. This compound possesses all the properties ascribed to the silicohydric chloride.

It has a vapour density of 4·64 (calc. 4·69). The product of its decomposition by water is by these authors stated to be silicic formanhydride, $Si_2H_2O_3$, analogous in constitution to the unknown formic anhydride

$$2SiHCl_3 3H_2O = 6HCl + (SiOH)_2O.$$

Silicic chloroform is decomposed by chlorine at ordinary temperatures, forming silicic chloride and hydrochloric acid.

Bromine does not act upon it below 100° (Friedel and Ladenburg, Bl. [2] 7, 322).

Silicon bromide $SiBr_4$ is produced by passing bromine-vapour over an intimate mixture of silica and charcoal, heated to redness in a porcelain tube. The product is purified by agitation with mercury and distillation. Colourless liquid, of a pungent odour. Sp.gr. = 2·813. It solidifies at 12–15° as an opaque white mass; b.p. =153·4; fumes strongly in air, and is decomposed by water.

It decomposes with detonation when heated with potassium.

Silicohydric bromide $Si_3H_4Br_{10}$, corresponding to the chloride, is obtained by passing hydrobromic acid gas over crystallised silicon and condensing the product. Purified by agitation with mercury.

It is a colourless liquid; sp.gr. 2·5; fumes strongly in the air, and is decomposed by water Wöhler and Buff (A. 104, 94).

Is probably a mixture of silicon bromide and silicon bromoform.

Silicon hexbromide Si_2Br_6, prepared by adding one equivalent bromine to a solution of the hexiodide in carbon disulphide; it crystallises in rhombic plates and is not isomorphous with the corresponding iodide (Friedel and Ladenburg, A. Ch. [5] 19, 390).

Silicon tetriodide SiI_4 is obtained by passing iodine vapour in a stream of carbon dioxide, through a long porcelain tube filled with silicon and heated to redness. The product sublimes in the cool part of the tube as a white crystalline mass. To purify it, it is dissolved in carbon bisulphide and agitated with mercury.

It crystallises by sublimation or from its solution in carbon bisulphide in colourless transparent regular octahedra; melts at 120·5° to a yellow liquid; boils about 200°, and distils unaltered in a stream of carbon dioxide. Vapour density = 19·12 at 360°. The vapour burns with a red flame, depositing iodine. It is decomposed by water and alcohol

$$SiI_4 + 2C_2H_6O = SiO_2 + 2C_2H_5I + 2HI$$

(Friedel, A. 149, 96).

Silicon triiodide Si_2I_6. When the tetriodide is heated to 300° with finely-divided silver, a white mass is obtained, which is purified by repeated treatment with small quantities of carbon bisulphide and ultimate solution with the aid of heat in that body.

On cooling, the tri-iodide separates out in colourless hexagonal prisms, which fume on exposure to air. It is decomposed by potash, forming silica, hydriodic acid, and free hydrogen.

It cannot be distilled, but may be partially sublimed, and readily decomposes.

It melts at 250° *in vacuo*, with partial decomposition.

With ice-cold water it forms a white mass having the composition $Si_2H_2O_4$ (silico-oxalic acid), which may be dried at 100°, but decomposes on heating with incandescence and loss of hydrogen.

Gently warmed with zinc ethyl it yields on distillation a mixture of silicon tetriethyl, b.p. 150–154°, and silicon triethyl, b.p. 250–253°, which may be separated by fractionation (Friedel and Ladenburg, C. R. 68, 920; Z. [2] 5, 289).

Hydrosilicic iodide is the name given by Wöhler and Buff to a compound formed by passing hydriodic acid over heated crystalline silicon (A. 104, 99).

This has been shown to be a mixture of silicic iodide, free iodine, and silicic iodoform $SiHI_3$ by Friedel and Ladenburg.

Silicic iodoform was prepared by them by passing hydriodic acid mixed with hydrogen over crystalline silicon.

It condenses together with free iodine, from which it may, with difficulty, be separated by distillation.

It is a colourless, strongly refracting liquid; sp.gr. = 3·362 at 0°, 3·314 at 20°; b.p. = 220°. It is decomposed by water in a similar manner to silicic chloroform (Friedel and Ladenburg, C. R. 68, 920; Z. [2] 5, 289).

Silicon hexiodide Si_2I_6. Prepared by heating silicon tetriodide with finely-divided silver in sealed tubes at 290–300° for several hours.

Si_2I_6 deposits on cooling in small hexagonal prisms, fuming in moist air, soluble in potash, hydrogen being evolved.

They may be fused in vacuo at 250°, undergoing partial decomposition (Friedel and Ladenburg, A. Ch. [5] 19, 390).

Silicon chlorobromides. A *trichlorobromide* $SiCl_3Br$ is obtained by the action of bromine upon silicic chloroform. It is a colourless, fuming liquid, boiling at 80° and decomposed by water. A *dichlorobromide* $SiCl_2Br_2$ is also formed in the above reaction, and is found amongst the products boiling at 100° (Friedel and Ladenburg, A. Ch. [4] 27, 416).

The *trichlorobromide* is also obtained without the second product by the action of Br upon the trichlorosulphydrate (Friedel and Ladenburg, *l.c.*).

$SiClBr_3$ was obtained by Reynolds from the tetrabromide (C. J. 1887, 590).

When pure dry thiocarbamide in fine powder is gently warmed with silicon tetrabromide, dissolved in benzene, combination slowly takes place, a compound being formed of the composition $SiBr_4 8(CSN_2H_4)$ (Reynolds, C. J. 1887, 202).

Silicon sulphide. The disulphide SiS_2 is produced by passing the vapour of carbon disulphide over a mixture of silica and lampblack made into balls and ignited. Silicon disulphide is deposited in the cold parts of the tube in asbestiform needles. It decomposes rapidly in contact with moist air, or aqueous vapour, forming hydrosulphuric acid and silica. Alcohol and ether act upon it in the cold. Nitric acid decomposes it, separating sulphur, and forming silica and sulphuric acid. Hydrogen has no action upon it (Fremy, A. Ch. [3] 38, 314).

SiS_2 is formed when dry H_2S is passed over crystallised silicon at a red heat, in fine white needles. A yellow sublimate is formed at the same time, probably consisting of Si_3S_4 (Sabatier, Bl. [2] 38, 153). Heat of formation of SiS_2 = +40·4 cals. (Sabatier, C. R. 90, 819).

A silico-hydric sulphide $Si_4H_8S_5$, corresponding to the oxygen-compound γ, is formed by the action of aqueous sulphurous acid mixed with a little hydrochloric acid upon calcium silicide. It separates in reddish-brown laminæ. It is dried *in vacuo*, and purified by treatment with carbon bisulphide. It smells persistently of sulphuretted hydrogen, burns like gunpowder, and explodes violently (with incandescence) when heated in a tube. With ammonia it gives off hydrogen, and is converted into a mixture of silica and sulphur (Wöhler, A. 127, 257).

A sulphochloride of silicon was obtained by Pierre, who gave it the formula $Si_3S_4Cl_8$, by passing a mixture of silicic chloride vapour and dry sulphuretted hydrogen gas through a red-hot porcelain tube, distilling the product, and collecting what passed over at 90°–100° (Pierre, A. 69, 73).

Friedel and Ladenburg assign to it the name *silicon chlorosulphydrate* and the formula $SiCl_3SH$ or *silicic mercaptan.* It is a colourless liquid, boiling at 96°, decomposing on exposure to the air into hydrochloric and sulphydric acids and silica. With alcohol, in the proportion of 3 mols. alcohol and 1 mol. of the body, it forms $SiSH(OC_2H_5)_3$, but an excess of alcohol converts it into silicic ether $Si(C_2H_5O)_4$.

With bromine it forms a trichlorobromide (Friedel and Ladenburg, A. Ch. [4] 27, 416; *v.* also Bl. [2] 7, 472).

SiS is formed together with SiSO, when carbon bisulphide is passed over silicon at a white heat. If the contents of the tube are treated with potash and hydrofluoric acid, a greenish powder is obtained having the composition Si_4C_4S, which is converted into $Si_4C_4O_2$ by heating in a current of oxygen (A. Colson, Bl. [2] 38, 56; C. R. 94, 1526).

Silicon nitride. Obtained by Deville and Wöhler by the action of ammonia on silicic chloride, and by exposing crystalline silicon to an intense heat in nitrogen or atmospheric air. It is a white amorphous infusible mass, which does not oxidise even on ignition with air, and is insoluble in all acids except hydrofluoric, which forms with it ammonium silicofluoride. It yields ammonium carbonate when ignited in a stream of aqueous vapour and carbon dioxide, and decomposes slowly, evolving ammonia in moist air. It is not acted on by aqueous alkalis. Fused with potassium hydrate, potassium silicate and ammonia are formed. Fused with potassium carbonate, it yields potassium silicate and cyanate. It reduces red oxide of lead with incandescence. Its composition has not been ascertained (Deville and Wöhler, A. 104, 256; 110, 248).

By heating crystalline silicon with gas-carbon in a blast furnace, a mixture, consisting of silica, together with a white and green substance, is formed. The green product is insoluble in hydrofluoric acid, and has the composition $(SiN)_x$. It is insoluble in water and caustic alkalis, but is dissolved by caustic potash at a red heat, potassium silicate being formed, hydrogen and ammonia being evolved. The white substance is soluble in hydrofluoric acid, and cannot be prepared in the pure state. Its composition is probably Si_3N_4 (Schützenberger, C. R. 89, 644).

When crystallised silicon is heated in a porcelain tube in an atmosphere of pure nitrogen a white mass is obtained, from which, by treatment with potash and hydrofluoric acid, a compound having the composition Si_2N_3 is obtained (Schützenberger and Colson, C. R. 93, 1,508).

SiCO is formed as a greenish powder when the residue obtained after heating crystallised silicon to whiteness in an atmosphere of carbonic acid is treated with hydrofluoric acid to remove silica. It is insoluble in acids and alkalis and oxidises with incandescence when heated with litharge (Schützenberger and Colson, C. R. 93, 1508).

Si_2C_2N is obtained when silicon (cryst.) is heated to whiteness in a brasqued crucible. It is a green-blue pulverulent mass, insoluble in acids or alkalis, and becomes incandescent when heated with litharge. It is also formed when crystallised silicon is heated in a current of cyanogen, or with carbon or a carbonaceous substance in an atmosphere of nitrogen (Schützenberger and Colson, *l.c.*).

When crystallised silicon is heated in a porcelain tube in an atmosphere of pure nitrogen, a white mass is obtained, from which Si_2N_3 may be prepared by treatment with caustic potash and hydrofluoric acid.

$Si_5N_6Cl_2$ is formed as a white powder when the product of the reaction of dry ammonia upon silicic chloride is heated to redness in a current of hydrogen. On heating this to redness in a current of ammonia it loses chlorine, and is converted into Si_2N_3H (Schützenberger and Colson, *l.c.*).

$SiCO_2$ is formed when ethylene or hydrogen, saturated with benzene, is passed over silicon in a porcelain tube. It is a whitish powder, unacted on by acids, chlorine, or oxygen.

Si_2C_3O is formed when carbonic acid is used in the above reaction instead of ethylene. $Si_2C_3O_2$ is also known. $Si_2C_4O_2$ is obtained by heating Si_4C_4S (*q. v.*) in a current of oxygen (A. Colson, Bl. [2] 38, 56; C. R. 94, 1526).

Metallic silicides. Silicon unites directly with aluminium, iron, zinc, platinum, and some other metals; not, however, with sodium, nor with lead or potassium. It dissolves in aluminium and zinc when heated, and separates out on cooling.

Calcium silicide ($CaSi_2$) is prepared as follows: 300 grs. of graphitoidal silicon and 3,000 grs. calcium chloride are intimately mixed in a hot mortar; the mixture is next agitated with 350 grs. sodium in small pieces, and introduced into a red-hot crucible containing a little fused common salt, and the whole covered with 350 grs. sodium, and lastly with a layer of fused and powdered common salt. The cover is put on, and the crucible heated to the melting-point of cast iron for half-an-hour. On cooling, the calcium silicide is found as a fused button, and must be preserved out of contact with air. It has a metallic lustre, lead-grey colour, scaly, crystalline structure; it crumbles on exposure to air. It is converted in chryseone by hydrochloric, acetic, or dilute sulphuric acids (Wöhler, A. 126, 257).

Cerium silicide, CaSi, is deposited, together with potassium, at the negative pole when a mixture of potassium fluoride and cerium oxide fused in a porcelain crucible is subjected to electrolysis. The potassium is removed with water, and cerium silicide remains as a brown powder, insoluble in acids, burning with a reddish flame. The silica is obtained from the crucible (Ulik, Z. [2] 2, 60).

Copper silicides.

A *white silicide* is formed in the preparation of silicon when silicon chloride vapour is passed over sodium heated in copper trays. It is very hard to the file.

Another silicide is obtained, containing 12 parts silicon to 88 parts copper, when potassic fluosilicate, sodium, and copper turnings are fused together. It is white, brittle, and more fusible than silver.

A third silicide is obtained by fusing the above with a larger quantity of copper. It contains 4·8 p.c. silicon, possesses a fine light bronze colour, is malleable, less hard than iron, and very ductile (Deville and Caron, A. 104, 232; A. Ch. [3] 67, 455).

A dark copper-coloured copper silicide is formed when copper sulphate is precipitated by siliciuretted hydrogen. It is readily oxidised, is decomposed at once by nitric acid, copper being deposited; it is soluble in hydrochloric acid, and decomposed by potash and ammonia.

Magnesium silicide. When magnesium chloride, sodium chloride, sodium fluosilicate, and metallic sodium are fused together for the preparation of siliciuretted hydrogen, the mass, besides free silicon, contains two magnesium silicides, one of which yields siliciuretted hydrogen when treated with sal ammoniac or hydrochloric acid, whilst the other yields hydrogen and silica (Wöhler, *l.c.*).

Platinum silicide. Platinum and silicon unite readily, forming a very fusible compound.

Potassium silicide. According to Berzelius, this body is formed when potassium fluosilicate is heated with potassium in the preparation of silicon. According to Deville, however, this is merely a mixture of potassium and free silicon.

Iron silicide. Silicon is almost always present in cast iron, owing to the deoxidation of silica in smelting. In white cast iron the amount varies from 0·1 to 0·5 p.c.; in grey, from 0·5 to 3 p.c. Iron obtained by the hot blast contains more than that produced by the cold blast.

Manganese silicide. Wöhler has prepared silicides of manganese containing silicon, varying from 11·4, 11·7, and 13 p.c., by fusing together manganese chloride and fluoride with silica or silicate or fluosilicates in varying proportions (A. 106, 54).

A **silicohydric selenide**, analogous to $Si_4H_8O_5$, was prepared by Wöhler by treating calcium silicide with selenious and hydrochloric acids. It has the colour of cinnabar, smells of seleniuretted hydrogen, is decomposed by ammonia, and splits up on heating into hydric selenide and selenium (Wöhler, A. 127, 257; J. 1863. 205).

For the organic compounds of silicon *v.* WATTS' DICTIONARY OF CHEMISTRY, new ed. by Morley and Muir.

SILICON BRONZE *v.* TIN.

SILK (*Soie*, Fr.; *Seide*, Ger.; apparently derived from the Chinese *Si*, or Corean *Soi*—the name of the silkworm) is the filament which the silkworm winds around itself as it assumes the chrysalis condition. It is a viscous secretion of the caterpillar, contained in two sacs, running one on each side throughout the length of the body. At the appointed time this is emitted through a twin-orifice in the under-lip, and immediately on contact with the air assumes a perfect hardness, the worm enveloping itself in its folds by a constant motion of the head. The silkworm from which the silk of commerce is mostly obtained is the mulberry-feeding larva of *Bombyx mori*, although many other caterpillars produce silk threads; owing to disease among the European stock, much attention has recently been turned to the latter. Of these it would appear that the Tussah worm *Antheræa pernyi*, feeding on various species of oak, ailanthus, &c., most nearly satisfies the requirements of the trade.

The thread is of varying thickness, according to the kind of worm producing it, and according to its position in the cocoon; but it may be taken as about one-thousandth part of an inch in diameter, and greatly exceeding any other textile fibre in strength.

The constituents of silk fibre are *fibroin*, coated with silk albumen or *sericin* and coloured ceraceous matter.

Fibroin $C_{15}H_{23}N_5O_6$ is a substance allied to horny tissue, and is obtained by exhausting silk with boiling water, alcohol, ether, and acetic acid successively. The silk after this treatment is very white, soft to the touch, and destitute of lustre. Fibroin when calcined emits the odour of burnt horn. By dry distillation it yields a large quantity of carbonate of ammonia, water, empyreumatic oil, and an abundant residue of charcoal. It does not dissolve in ammonia or in alkaline carbonates, but is soluble in sulphuric acid, hydrochloric acid, nitric acid, and phosphoric acid.

Sericin $C_{15}H_{25}N_5O_8$ is a gelatinous substance, soluble in weak alkaline solutions and in hot water, with which, on cooling, it forms a strong jelly. It is precipitated as a white powder by alcohol. The yellow colouring matter of raw silk consists of *chlorophyll*, more or less altered and deprived of its blue constituent. From the greenish cocoon unaltered chlorophyll may be extracted. For the cultivation and manufacture of silk *v.* Ure, vol. iii.; Ency. Brit. 9th ed. vol. xxii. 56.

SILK GREEN. *Chrome green v.* CHROMIUM; also PIGMENTS.

SILVER. Ag (*Argentum*). At. wt. 107·66. The knowledge of this metal dates from the remotest antiquity, and the earliest records refer to its use as a medium of exchange. In colour, silver is whiter than any other common metal or alloy, and it is capable of receiving a brilliant polish. It crystallises in the cubical system, and fine octahedra are occasionally observed. When subjected to mechanical stress, silver is very 'tough' and possesses a somewhat high tensile strength, a wire one square millimetre (0·0016 square inch) in section breaking at 0°C. under a stress equal to 17·27 tons per square inch. At higher temperatures the tensile strength diminishes, being 14·19 tons per square inch at 100°C. and 11·33 tons at 200°C. The metal is exceedingly malleable—more so, indeed, than any other metal except gold. It may be hammered into leaves but $\frac{1}{10000}$ of an inch in thickness, and a single grain of it may be drawn into a wire 400 feet in length. It is hardened by hammering or rolling, but recovers its malleability by annealing at a low heat. Silver is slightly harder than gold ($2\frac{1}{2}$), and is considerably softer than copper. Its specific gravity is variously given at from 10·304 to 10·6139, according to the methods of preparation and treatment. When molten, it has the specific gravity 9·461. The specific heat of silver is 0·05701, and Pionchon gives the latent heat of fusion at −24·72 calories for 1 gramme. Silver has a higher conductivity for heat and electricity than has any other metal, and has therefore been adopted as the standard for comparison. If the conductivity of the hard-drawn wire is taken as 100, that of the annealed wire will be 110. Silver melts at 954°, and may readily be volatilised, the volatilisation commencing in a current of hydrogen at about the melting-point of copper. When in the form of a very thin film, silver appears transparent, and transmits blue light.

The softness of silver and the consequent 'wear' of the metal when in use, led even in very early times to the addition of some other metal for the purpose of hardening it, and thus rendering it more suitable for commercial purposes. Such a hardening effect is produced by copper, and the silver coins of Britain from Saxon times to the present day have consisted of such an alloy in the proportion of 925 parts of silver to 75 of copper.

Silver ornaments, in the course of hundreds of years, are found to become crystalline and very brittle, the specific gravity diminishing considerably, but the metal resumes its original properties on annealing. When molten, silver absorbs 22 times its volume of oxygen, but on solidification the whole of this is liberated again with the exception of 0·7 volume. Comparatively small quantities of foreign metals prevent this occlusion of oxygen.

Silver ores.—The following are the more important: Native silver 97–99·8 p.c. Ag; the antimonide (*dyscrasite*), Ag_2Sb–Ag_6Sb; the telluride (*hessite*), Ag_2Te; the sulphide (*argentite*), Ag_2S; brittle silver ore (*stephanite*), $5Ag_2S,Sb_2S_3$–68·3 Ag; ruby silver ore (*pyrargerite*), $3Ag_2S,Sb_2S_3$-60Ag; light-red silver ore (*proustite*) $3Ag_2S,As_2S_3$–65·4 Ag; *polybasite* $(Cu_2S,Ag_2S)_9(Sb_2S_3,As_2S_3)$–64–72 Ag and 10–3 Cu; fahl ore (grey copper ore), either a complex antimonio-sulphide, arsenio-sulphide, or antimonio-arsenio-sulphide, containing variable quantities of silver, occasionally exceeding 30 p.c.; *stromeyerite*, Cu_2S,Ag_2S–53·1 Ag; *horn silver*, AgCl; the iodide and bromide; and amalgams of varying composition.

Most ores of lead contain silver; indeed, this metal is of such constant occurrence with lead, that ores of the latter metal form one of the main sources of production of silver. Silver is also frequently present in ores of zinc and copper, and considerable quantities of the precious metal are annually derived from this source. It is also found occasionally in ores of iron. In the following table some of the more important silver ores are arranged according to their relative degrees of hardness:—

Name	Colour	Lustre	Streak	Hardness	Sp.gr.
Horn silver	Grey, brown, green	Resinous	White, light grey	$1\frac{1}{2}$	5·3–5·6
Tellurides	Light grey, iron black	Metallic	Light grey, iron black	$1\frac{1}{2}$–$2\frac{1}{2}$	7·5–9·4
Argentite	Grey black	,,	Dark grey, lustrous	$2\frac{1}{2}$	7·2–7·4
Polybasite	Iron black	,,	Iron black	$2\frac{1}{2}$	6·1–6·3
Stephanite	,, ,,	,,	Grey black	$2\frac{1}{2}$	6·3
Proustite	Cochineal red	Adamantine	Cochineal red	$2\frac{1}{4}$	5·4–5·6
Pyrargerite	Dark red	,, ,,	Brown red, cherry red	3	5·7–5·9
(Amalgam	Silver white	Metallic	Grey	$3\frac{1}{4}$	10·8)
Dyscrasite	,, ,,	,,	,,	$3\frac{1}{2}$	9·7
Tetrahedrite	Steel grey	,,	Grey, black	$3\frac{1}{2}$	4·5–5·2

In view of the widespread presence of silver in other ores, its metallurgy is, perhaps, more varied than that of any other metal. Thus certain of the ores of silver are readily decomposed by mercury direct, whilst others must first be submitted to a preliminary metallurgical treatment before being amalgamated. Others, again, are altogether unsuited for treatment by mercury, and smelting in admixture with ores of lead or of copper must be adopted, or a 'wet' process must be employed.

These various processes may be classified as follows:—

I. Amalgamation.
II. Wet processes.
III. Treatment by metallic lead.
IV. Smelting in conjunction with ores of lead or of copper, or with iron pyrites.

Amalgamation methods depend on the decomposing action exerted by mercury on certain compounds of silver and gold, together with the solubility of these metals in the mercury used in the process. If, then, the precious metals exist in the ore to be treated in some form which is not readily attacked by mercury, some preliminary process is necessary for the purpose of changing this into another form which mercury will readily decompose. In the case of silver, this subsidiary process usually consists in roasting with common salt at elevated temperatures, but in one of the older methods a mixture of common salt and a salt of copper is employed, which produces the same effect at a temperature not exceeding that of a tropical summer. This process, the Mexican patio process, is, at present, of minor importance, and may soon be of little more than historical interest. It is still, however, in use in Mexico and South America, and deserves to be mentioned. It is stated to have been invented by Bartholome Medina, a native of Pachuca, Mexico, in 1557, and has undergone practically no change since that date. The ore, as it comes from the mines, is first broken down to a small size in a stamp battery of primitive type, and is then ground to a fine powder in an 'arrastra,' a circular space 12 or 15 feet in diameter paved with hard stone. In the centre of this arrastra is a pivoted vertical beam supporting a series of horizontal arms. These arms are connected by thongs to heavy stone blocks, and are caused to revolve, usually by mule power. The grinding of the ore charged into such an appliance is effective, though slow. If much free gold and silver or halogen compounds of silver are present, mercury is charged into the arrastra for the purpose of collecting the precious metals at this stage.

The next stage of the process is to convey the finely-ground ore, when in the form of a thick mud, to the 'patio,' or amalgamating floor, which consists, as a rule, of a circular paved space some 40 or 50 feet in diameter. On this the ore mud is spread to a thickness of about a foot, from 3 to 5 p.c. of common salt is added, and is well mixed with the ore by being trodden in by mules driven round and round over the heap. Various mechanical devices have been invented to do away with the use of mules for this purpose, but, the process having survived mainly through its simplicity, these mechanical mixers have never come much into use. After the salt has been stirred in, about a day being occupied in this manner, mercury and 'magistral' are added. Magistral consists mainly of a mixture of the sulphates of copper and iron, and is usually produced by roasting copper pyrites in a reverberatory furnace. The following are analyses of such a product:—

	$CuSO_4$	CuO	$FeSO_4$	Fe_2O_3	SiO_2
I.	9·03	5·00	6·75	18·75	60·47
II.	19·00	5·50	14·80	25·80	34·90

The magistral is scattered evenly over the surface of the heap, and is then thoroughly incorporated with the ore by mixing it in with wooden shovels. The heap is stirred at intervals for some days. Mercury is next sprinkled over the mass under treatment, in the proportion of from 6 to 8 parts of mercury for every 1 part of silver present. Immediately after the addition of the mercury, the mass is again trodden and stirred for about two hours. A hot solution of copper sulphate is then added to the pile, the quantity so added being the larger the more sulphur, arsenic, antimony, and zinc are present. Copper precipitate is also added in the proportion of one part of copper to five of the sulphate. The heap or 'torta' is again trodden for some hours. The reactions in the 'torta' commence immediately after the addition of the magistral, but some days elapse after the addition of the mercury before the reaction is complete. Fresh mercury is then sprinkled over the charge, and the amalgam is collected by stirring the mass, with the addition of water, in a settler. The amalgam collects at the bottom of the settler, is run off, pressed, and the solid amalgam treated as in the case of Gold (*q.v.*).

The reactions in this process are very complicated, and have given rise to much discussion. They may possibly involve the formation of the chlorides of copper, which, in turn, react on the sulphides, sulph-arsenides, and other compounds of silver present, forming silver chloride, which is then reduced by the mercury added. The formation of silver chloride has, however, been denied. (For a full account of this process and its modifications, see Egleston, Metallurgy of Silver, Gold, and Mercury in the United States, 1887, vol. i. 261, &c.)

Another form of amalgamation, which is now only occasionally employed, is the barrel process. This appears to have originated at Freiberg, in Saxony, and was in use there until 1866, when it was abandoned in favour of smelting with ores of lead. In its main features the process consists in (1) crushing and grinding the ore; (2) roasting the crushed ore with salt; (3) amalgamating the roasted ore in barrels; and (4) collecting and distilling the amalgam, and melting the resulting metal. The ore as it comes from the mine is put through some form of drying furnace—usually a rotating cylinder—and is then passed through a Blake, Dodge, or other form of crushing machine. It is next roasted with salt, or is first subjected to a fine grinding. The roasting is performed in the same manner as in 'pan amalgamation,' the various silver compounds being changed by this treatment into silver chloride. The roasted ore is then charged into a series of barrels mounted on trunnions and capable of being rotated. A charge for a barrel would consist of about 2,000 lbs. of ore, and from 60 to 150 lbs. of iron scrap. Water is then immediately added, in quantity just sufficient to moisten the ore, and the barrel is rotated at the rate of about 12 to 14 turns a minute for a period of some 4 hours. The rotation is then stopped, and the charge of mercury is introduced, a small quantity of copper sulphate being also occasionally added. About 2 lbs. of mercury is added for every ounce of silver contained in the ore. The rotation is then recommenced and continued for some 16 hours, when, if it is found that the mercury has been well and evenly disseminated through the pulp, the barrel is nearly filled with water, and again rotated, in order to collect the mercury. If, however, when the barrel is first opened, the mercury is found to have collected in a body, and not to have disseminated itself through the charge, a further period of rotation will be necessary, and it may be desirable to thicken the pulp. On the other hand, the rotation may have been too long, and the mercury may have become floured. In this case fresh mercury must be added and the barrel rotated, with the view of collecting any mercury that may have been too finely divided by the previous treatment.

After filling the barrel with water, the rotation is continued for about an hour, when the mercury and amalgam at the bottom of the barrel are run off. Fresh mercury (about 100 lbs.) is then charged in, and the barrel again rotated slowly for an hour, with a view to collect any additional mercury that may have been retained in the pulp. This second charge of mercury is then drawn off as before, and the remainder of the contents of the barrel is discharged into a settler, a vessel provided with some means for stirring, such, for instance, as rotating arms. Any residual mercury collects here, and the rest of the ore residues is either subjected to a further concentration, or is allowed to flow away.

The amalgam is strained and retorted in the ordinary manner, the mercury being used again for the next charge, as that portion derived from the straining of the amalgam contains appreciable quantities of silver, and, it may be, gold.

The barrels used in this process may have the following dimensions: length and diameter, each $4\frac{1}{2}$ feet. They may be made with staves 5 to $5\frac{1}{2}$ inches wide, and $3\frac{1}{2}$ to 6 inches thick, hooped and tied with iron.

The Cazo process forms an intermediary stage between the arrastra and the more modern pan process. Like the latter, it consists in treating the ore to be amalgamated in a receptacle provided with a metal bottom; but it also resembles the former to some extent in its general character. The ore to be treated is first ground fine in an arrastra. Instead, however, of being then amalgamated in the patio it is transferred to a receptacle having a copper bottom, heated from below. The charge consists of a very variable quantity of ore, made into a paste with water, some 5–10 p.c. of salt being also added. Heat being supplied, mercury is charged in, and the mass stirred for some hours, until the amalgamation is believed to be complete. After dilution with water and settling, the mercury is drawn off and the slimes are transferred to settling tanks. After settling, the slimes may be treated over again in a patio. This process is still employed at, perhaps, the largest silver mine in South America—at Huanchaca; and a description of the process as there employed will be found in the Oesterreichische Zeitschrift für Berg- und Hüttenwesen, vol. xxxviii. (1890), 269.

All these older forms of amalgamation have now, in the great majority of cases, given place to the simpler form of 'pan' amalgamation.

In this process the ore is broken down to a size suitable for treatment (with water) in a stamp battery by the aid of a stone crusher, and is then crushed to a variable degree of fineness, a 30-mesh screen being usually employed. The fine mud passing through the screens is allowed to deposit in a series of settling tanks, being sometimes in the first instance passed over amalgamated copper-plates, to collect any free gold that may be present.

The mud deposited in this manner is then charged into iron 'pans,' in which it undergoes a further grinding, followed by amalgamation. These pans are of very varied form. Gradually, however, the more complicated varieties have been replaced by others of more simple construction. In principle they all consist of a fixed and a rotating iron plate, which may be so arranged as to serve either for grinding or for mixing the ore with mercury. Through the centre of the bottom and fixed plate rises a hollow pillar, within which is an upright shaft, projecting above the pillar, and giving motion to the upper and revolving grinding-plate. Both this plate and the fixed one are provided with reversible wearing faces—'shoes' and 'dies.' This arrangement is shown in the accompanying diagram of the Patton pan (fig. 1). The charging is performed by raising the upper revolving plate—the 'muller,' with its 'shoe'—setting it in motion, and then running in a little water and the mud from the settling-tanks, the charge being brought to the consistency of a thick paste. The pan is usually provided with a hollow jacket or bottom, into which steam can be injected; and this is done at this stage. The muller is now lowered sufficiently to grind the charge against the bottom plate, and the grinding is continued until the pulp when rubbed between the finger and the thumb shows little trace of grittiness. When this stage has been reached (in two or three hours) the muller is raised a little and mercury is charged in. It is evident that the more finely disseminated is the mercury in the charge of ore the more perfect will be the amalgamation; and this is best accomplished by squeezing the mercury—in part, at least—through a bag in such a manner as to allow it to fall in a series of fine jets towards the outer edge of the revolving muller. The charge of mercury varies considerably, a portion remaining, as a rule, continuously in the pan throughout the campaign, a separate addition being made with each charge.

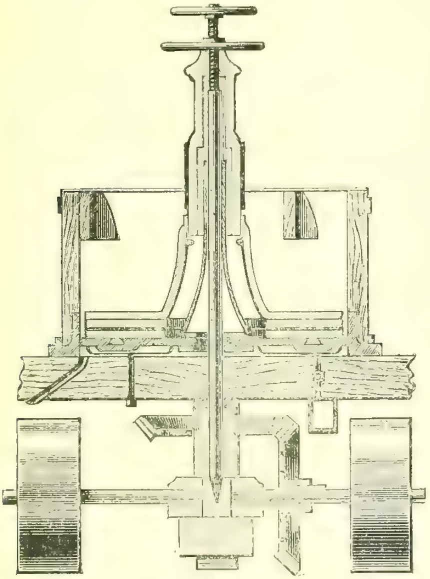


Fig. 1.

The raising of the muller during the amalgamation stage is for the purpose not only of allowing it to act as a stirrer, but also to avoid the reduction of the mercury to such a degree of fineness as to prevent its recovery in the third stage of the process—to prevent, that is, the 'flouring' of the mercury.

The amalgamation stage lasts for two or three hours. If properly performed, a portion of the ore taken from the pan and rubbed with the finger on a flat piece of wood should then show some small globules of mercury. When the amalgamation is deemed complete, water is charged into the pan, and, the muller being raised still further and kept in revolution, the charge is brought to the condition of a thin mud. This is then run off through an orifice at the lower part of the pan into a larger pan of somewhat similar form, termed a 'settler.' This differs from the 'pan,' in that it carries instead of a revolving grinding surface a revolving stirrer. In this settler the charge is largely diluted with water, and, the stirrer slowly revolving, the mercury collects and 'settles' at the bottom. Whilst, however, the dilution should be complete enough to allow the mercury to collect, if it be carried too far the coarser particles of the mud will also settle—and this must be avoided. The settlers are usually arranged immediately below the pans, in such a manner that the settler receives the contents of two pans. The arrangement of pan and settler is shown in figs. 2, 6, 7, 8, and 9.

Fig. 2 shows the arrangement of the experimental plant at the Royal College of Science.

The mercury collected in this manner is either taken to a smaller or 'clean-up' pan, where it receives a further treatment with water to free it from grit and to clean the mercury, or is taken direct to strainers—conical canvas bags—where the fluid amalgam is strained away from the richer solid amalgam remaining on the strainers. The fluid amalgam passing through the strainers, representing the saturated solution of the solid amalgam in the excess of mercury employed, is relatively poor in the precious metals. This is returned to the pans for the next charge.

The solid amalgam is pressed to free it from any remaining mercury, and is then 'retorted' in iron retorts, the mercury condensed in water-cooled pipes, and the silver and gold, which still retain some mercury, melted down in crucibles, and cast into bars.

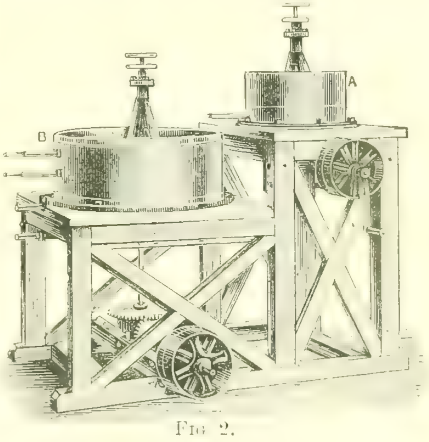


Fig. 2.

The thin mud escaping from the settler is usually re-treated in a larger form of settler, termed an 'agitator,' and is then passed over blanket sluices, vanners, or other similar arrangements for the purpose of collecting the heavier pyrites, usually rich in gold and silver, and some of the mercury which may have been too finely disseminated to admit of its being collected in the settler.

The above is a description of the process in its simplest form. It has, however, one important modification, and several minor ones. Amongst these latter may be mentioned the customary addition of a small quantity of copper sulphate and common salt to the charge in the pan. It is difficult to understand the action of this addition chemically; possibly, however, it may consist in aiding in the formation of an amalgamated surface on the iron of the pan exposed to the action of the charge, or in assisting in keeping the mercury 'lively.' Another consists in the occasional use of copper sides to the pan in cases where ores very rich in copper are being treated, and which would otherwise cause a rapid corrosion of an iron pan. The important modification of the process referred to consists in first drying the ore, followed by a roasting operation, by which, salt being added, the silver sulphide and other compounds present in the ore are converted into chloride, a compound which is readily treated by the pan process. This roasting process necessitates the use of dry-crushing stamps, instead of the wet-crushing stamps otherwise employed, and thus greatly reduces the 'capacity' of the mill for a given number of stamps, to about one-half or one-third. Again, the roasting process may in itself occasionally lead to considerable loss in gold, owing to the conversion of the gold into some form soluble in water, and which escapes complete reduction in the after-treatment in the pans. The silver, too, if an insufficient quantity of decomposable sulphates is produced in the roasting, may not be completely converted into chloride, but this roasting process will be further dealt with when describing the leaching process for the treatment of silver ores.

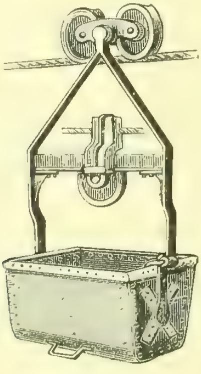


Fig. 3.

The dry process possesses the advantage over the simpler wet process of a largely increased yield of the precious metals contained in the ore, but against this must be placed increased cost of treatment and the largely reduced capacity of the plant, accompanied by an increased first cost. It is evident, therefore, that the choice of one or other of the two processes must depend not only on the nature of the ore to be treated, but to a very large extent on the local conditions under which such treatment would have to be carried out.

Difficulties connected with the water supply frequently render it necessary to place the mill at some distance from the mine. The transport of the ore from the mine to the mill is then effected either by teaming, by a tramway, or by a wire ropeway. In mountainous regions this latter is frequently preferable. There are various systems. In the Otto system the buckets run on a fixed rope, and are drawn forwards by a lighter haulage rope as is shown in fig. 3.

A general view of the ropeway when erected is shown in fig. 4.

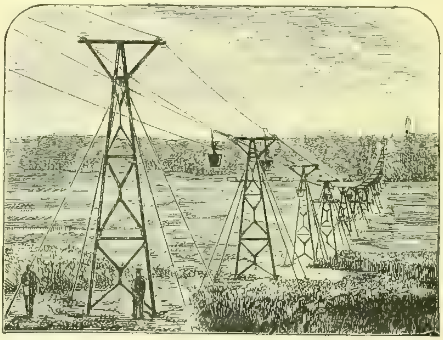


Fig. 4.

The ore is delivered from the buckets to the stone-crusher. This is best placed immediately above the ore-bins, into which the crushed ore falls by gravity. The stone-crusher is usually a modification of the Blake type, fig. 5.

When ore-bins are not erected the crusher is placed behind the stamps as is shown in fig. 9, or behind fast-running and fine-crushing rolls when these are used in the place of a stamp battery. For coarse crushing silver ores rolls possess some advantages over a stamp battery, which have already been referred to (*v.* Gold).

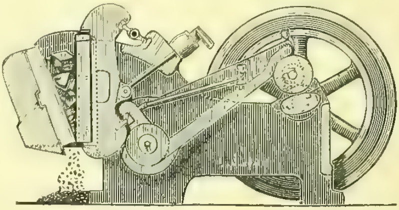


Fig. 5.

The ore-bins in a wet-crushing mill deliver the crushed ore directly to the stamps. In a dry-crushing mill the ore is delivered to the drier, which is placed above and behind the stamps, the main aim in designing the position of the plant being to diminish the hand labour required. The position of the various portions of the plant in a wet and in a dry crushing pan amalgamation mill is shown in detail in figs. 6, 7, 8, and 9. For these designs the writer is indebted to Messrs. Commans & Co., of London, E.C.; fig. 6 is a dry-crushing mill. In this no bins are shown, the ore delivering on a floor immediately above the self-feeder of the stamp battery (either a direct carrier or a shaking table worked by the stamps).

Fig. 7 shows the front view of a dry-crushing mill, and fig. 8 a plan.

Fig. 9 is a section through a mill arranged for wet-crushing.

Instead of the blanket sluices and vanners, to which reference has been made, as a means for saving the heavy sulphides escaping in the tailings from the agitators, the Cornish buddle, fig. 10, may be employed with advantage.

The buddle, too, is occasionally of very great importance as affording a possibility of effecting the concentration of a silver ore in cases when more modern appliances, such as the Frue vanner, give very unsatisfactory results. Thus in the case of ores containing tetrahedrite (grey copper ore) rich in silver, attempts at wet concentration are almost always failures, except in those cases in which a buddle is employed, but even this does not always give satisfactory results in the treatment of such ores, the tetrahedrite floating away with the tailings.

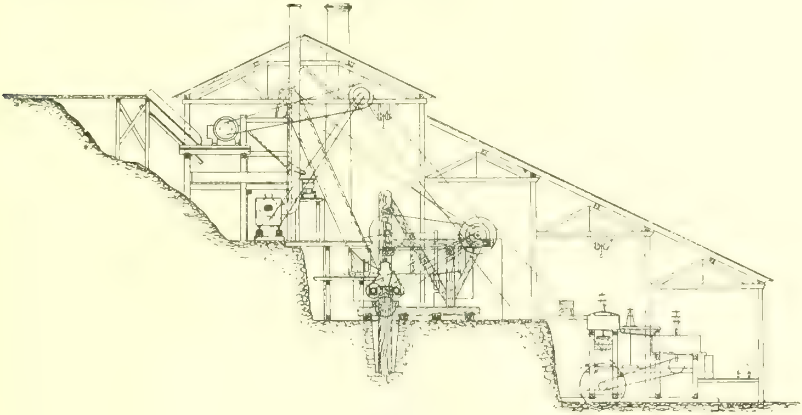


Fig. 6.

With regard to the machinery in use, the stamps in a wet-crushing mill are arranged as in a battery crushing auriferous quartz, though the screens used are, as a rule, somewhat coarser. The various remarks relating to a stamp battery in the article on Gold are, therefore, equally applicable in this case. When the battery is crushing dry, the whole of the screens are covered in, and the crushed ore conveyed away by belts or screw conveyers. Fig. 11 shows the arrangement of a dry-crushing battery which would be provided with such a screw conveyer.

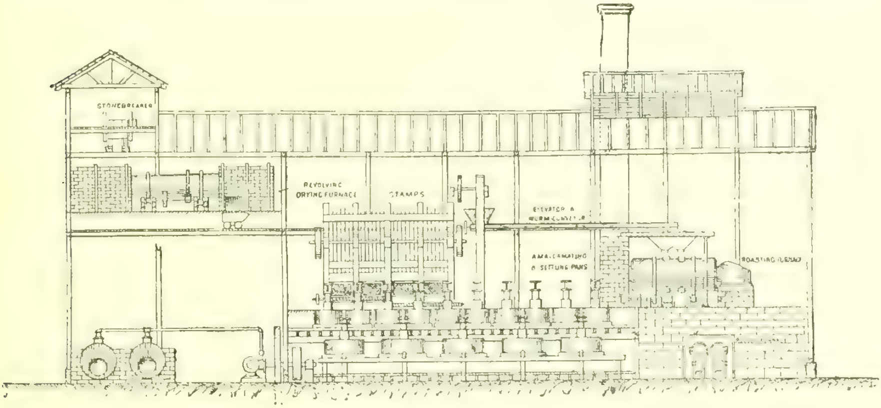


Fig. 7.

The *pans* have a capacity of from 1,500 lbs. to 4,000 lbs. In dry-crushing mills they are placed in front of and below the stamps; in wet-crushing mills their position is in front of the settling tanks. Pans are sometimes made wholly of iron, but they have frequently wooden sides, occasionally protected on the outside by sheet iron. A five-foot pan, 40 inches deep, with wooden staves, weighs about 6,500 lbs., whilst if made entirely of iron it will weigh about 7,000 lbs. They may be made in sections not exceeding 300 lbs. in weight, for mountain transport. In operation, the charge is made into a very thick paste, sometimes almost as thick as the muller will move in; the temperature of the charge is kept at from 80° to 95°C. To secure the best grinding the pulp should be thin, to secure the best amalgamation it should be as thick as honey; it is therefore better to have the pulp somewhat thin at the beginning and thickened towards the end of the grinding. The charge is usually in the pan about five hours. The quantity of mercury charged varies with the mode of operation and with the richness of the ore, from about 200 to 500 lbs. It is usually about 10 p.c. of the weight of the ore, and is pressed into the charge in a fine stream, either through canvas, or through a strainer, as already described. A little sodium or zinc is sometimes added to 'quicken' the mercury, and potassium cyanide is also used for this purpose. The loss of mercury is about 2 lbs. per ton of ore. The pan loses in weight by the wearing down of the shoes and dies &c. about 7 to 10 lbs. of iron per ton of ore treated as compared with 2 to 3 lbs. of iron in the batteries. Common salt and copper sulphate are, as stated, usually added in small quantities.

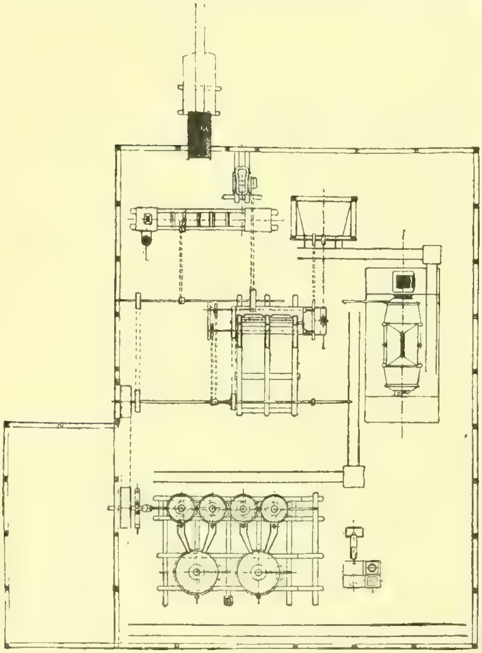


Fig. 8.

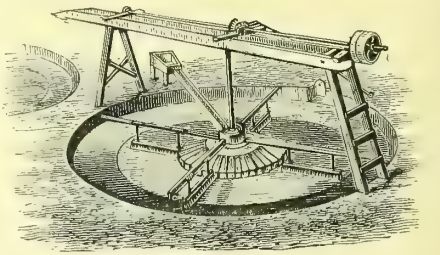


Fig. 10.

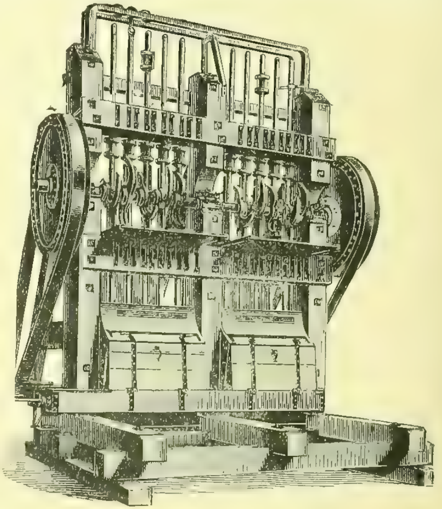


Fig. 11.

An eight-foot 'settler,' three feet in depth, will weigh about 7,000 lbs. The mercury is never completely removed from it except at the end of the mill run, about 100 lbs. being always left in the receiver. The settlers connect with sluices leading to the agitators; about one agitator serving for

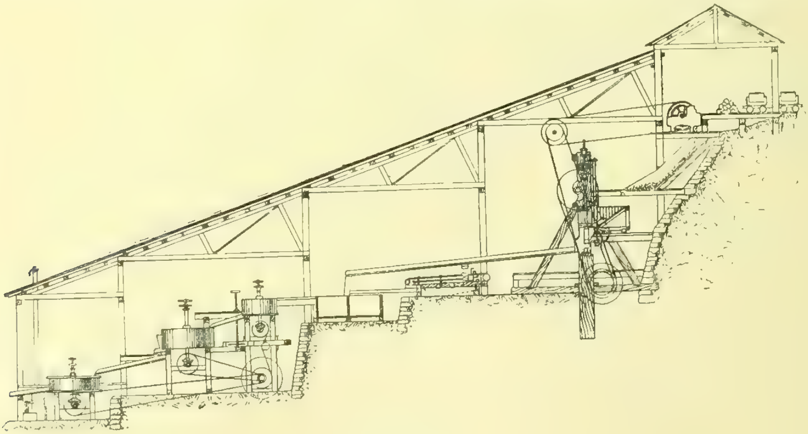


Fig. 9.

five or six settlers. They are of wood, from 8 to 20 feet in diameter and from 2½ to 4 feet deep. The tailings from the agitators are usually run over blanket sluices, vanners, buddles, or other forms of concentrating appliances.

The muller in a pan rotates about eighty times per minute, the arms of the settler about 10 to 15 times, and those of the agitator about the same number. For every battery of five stamps two pans would be required. The following table (Egleston, Silver, p. 443) shows the horse-power required for various mills:—

—	Wet-crushing Mills						Dry-crushing Mills	
	10 Stamps		20 Stamps		60 Stamps		10 Stamps	
	Number	H.-P. required	Number	H.-P. required	Number	H.-P. required	Number	H.-P. required
Blake crusher, No. 2. . .	1	6	1	6	1	5½	1	6
Ore feeders	2	0	4	0	—	—	2	0
750 lb.-stamps, 90 drops .	10	12	20	23	60	67½	10	12
40-in. rotatory furnace .	—	—	—	—	—	—	1	4
5-ft. pans	6	30	12	60	28	112	4	8
8-ft. settlers	3	9	6	18	14	28	2	8
Concentrators	—	—	—	—	3	6	—	
Friction	—	7	—	13	—	25	—	9
Total horse-power . .	—	64	—	120	—	244	—	47
Tons of ore treated per day	—	20	—	40	—	140	—	18

The engines should be of at least double the horse-power theoretically required.

The roasting furnaces employed in dry-crushing silver mills are usually of the revolving cylinder type, of which the Robey form of Brückner furnace is shown in fig. 12.

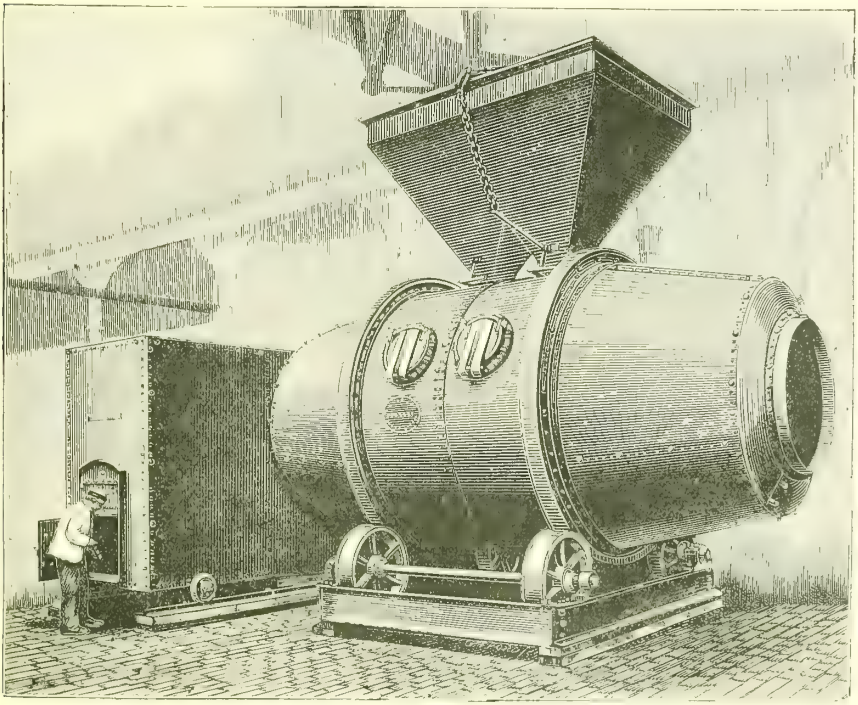


Fig. 12.

A 60-stamp wet mill requires about 1,400 gallons of water per minute; this can be regained, less 20 p.c. loss.

The following are the actual working expenses of a dry-crushing mill treating 50 tons of ore a day (Trans. Amer. Inst. Min. Eng. 8, 557):—

No. of men employed	Wages per day	Wages per ton of ore treated
	Dollars	Dollars
1 Foreman	10	0·20
1 Assayer	6	0·12
3 Machinists	12	0·24
2 Carpenters	8	0·16
2 Blacksmiths	8	0·16
2 Engineers	8	0·16
2 Foremen	7	0·14
9 Drying floor men	31½	0·63
3 Battery men	12	0·24
6 Roasters	24	0·48
12 Cooling floor men	48	0·96
4 Car men	16	0·32
4 Amalgamators	18	0·36
1 Retorter	4	0·08
1 Melter	4	0·08
4 Labourers	10	0·20
4 Watchmen	12	0·24
2 Ore floor men	7	0·14
3 Clerks	12	0·24
66	257½	5·15

The cost of supplies was as follows:—

	Dollars	Per ton of ore Dollars
Salt, 10 tons	80	1·60
Mercury, 175 lbs.	87½	1·75
Wood, 15 cords	67½	3·53
Coal, 12 tons	99	
Castings		1·50
Oil and waste		0·25
Sundries, chemicals, &c.		0·50
Hauling from mine		0·49
Charcoal, assaying and melting		0·25
Total		9·87

or a total and somewhat extravagant cost of 15·02 dollars per ton of ore treated in the mill.

As the wet process does not involve either drying or roasting, it will be seen from the above how greatly the cost of labour is diminished by the use of the wet process in the place of the dry method, and as the output of the stamps is at the same time trebled, the lesser yield is frequently a matter of relative indifference.

The following table gives details relating to the plant and process adopted at some other pan amalgamation silver mills:—

—	1	2	3	4	5	6
Character of Process	Wet	Wet	Wet	Dry	Dry	Dry
Number of stamps	80	20	30	15	40	50
Weight ,, ,, lbs.	—	650	700	850	800	850
Drop ,, ,, inches	8	8½	—	8½	8½	7
Number of drops per minute	100	90	80	63	92	—
Ore crushed per day, tons	320	45	—	—	55	250
Men employed at battery	12	—	—	—	3	—
Number of pans	44	16	14	8	24	20
Charge of pan: ore, lbs.	3600	1200	2800	1500	2500	3600
,, ,, ,, salt, lbs.	18	10	—	—	25	18
,, ,, ,, copper sulphate, lbs.	6	2	—	—	—	6
,, ,, ,, mercury, lbs.	350	200	—	—	300	350
Time ground before charging mercury, hours	3½	2½	—	—	1	—
Time amalgamated after charging mercury, hours	1½	3	—	—	6	—
Number of settlers	20	16	7	4	12	10

Vertical furnaces have been introduced into practice, with, in some cases, considerable success, by Stetefeldt and others, and long-bedded reverberatory furnaces are also in common use in places where labour is not expensive. The cost of the process varies up to about 5*l.* a ton, according mainly to the capacity of the plant, the cost of transport and the rate of wages, dry crushing being on the whole about 50 p.c. dearer than the wet process. The yield by value is about 90 p.c. as compared with 75 p.c.

Wet processes for the treatment of silver ores and argentiferous products are for the most part based on the solution of silver chloride by some solvent, such as common salt, sodium or calcium hyposulphite (thiosulphate), followed by the precipitation of the silver either in the metallic form or as a sulphide. This treatment usually involves the roasting of the ore with salt to convert the silver into the soluble form.

A still simpler method consists in the conversion of the silver not into chloride but into sulphate, this salt being then extracted by water, and the silver precipitated from its solution by replacement by a cheaper metal. This process is known as the 'Ziervogel' method, and the following is a description of the process as employed at a works in Colorado. It is based on the fact that when a mixture of the sulphates of iron, copper, and silver is raised gradually to a high temperature, the sulphates are not decomposed simultaneously, but gradually, with the increasing temperature in the order named. Thus, while the whole of the iron sulphate may have been converted into oxide, the whole of the silver sulphate and a portion of the copper sulphate will remain unchanged, and may be extracted from the roasted mass by the solvent action of water. At the works referred to, the ores treated average about 50 oz. of silver, 0·75 oz. gold, and 2·5 p.c. of copper. About 90 p.c. of the ore treated contains no copper. The process employed consists in producing a regulus containing about 40 p.c. of copper, 400 oz. of silver, and 6 oz. of gold per ton. This regulus may also contain up to 10 p.c. or more of lead.

The next operation is to roast this 'bronze metal,' and, melting it down with rich siliceous silver ores, to produce a 'blue metal' containing some 60 p.c. of copper with 750 oz. of silver and 10 oz. of gold per ton. This is then subjected to the Ziervogel process. After being crushed to such a size that it will pass through a screen of 6 meshes to the inch, the greater part of the sulphur is driven off by a prolonged roasting. When cold, the roasted charge is ground to such a degree of fineness that it will pass through a 60-mesh screen. It is then roasted at a low temperature for about 1½ hour; the temperature is then raised slightly for a similar period, copper sulphate being formed, the roasting charge increasing in bulk. The roasting is then continued at a slightly higher temperature for a like period, during which the silver is converted into sulphate, and care taken by frequent stirring to convert any cuprous oxide remaining from the decomposition of the copper sulphate into cupric oxide, as it would otherwise throw down metallic silver during the lixiviation.

The next operation is to leach the roasted ore with water, in order to dissolve the silver sulphate and any residual copper sulphate it may contain. The solution is passed through a number of vats, arranged in series and filled with copper scrap. This throws down the silver, replacing it in the solution, which is then passed over iron scrap to throw down the copper. The precipitated silver is freed from copper by the aid of dilute sulphuric acid.

The residues from this treatment are still rich in silver, partly owing to incomplete sulphating and partly owing to the formation of insoluble compounds of silver with antimony, arsenic, and, especially, bismuth. They contain about 40 oz. of silver, 10 oz. of gold, and 55 p.c. of copper per ton, together with sulphate of lead and bismuth, ferric oxide, &c. They are fused with pyritic ores, for the production of a regulus containing 65 p.c. of copper, 10 to 15 oz. of gold, and 80 oz. of silver per ton. The further treatment consists in best selecting (*v.* Copper) to obtain bottoms rich in gold and silver which may be treated by electrolytic methods, by the action of sulphur, or by acids; these bottoms contain about 150 oz. of gold and 300 oz. of silver per ton. The residual regulus is treated by the Ziervogel process as before.

At a Welsh works, copper bottoms similar to those above described, though poorer in the precious metals, are treated in the following manner: The molten metal, containing a little sulphur, is poured into water for the purpose of producing hollow granules. These are first roasted carefully to oxide, then ground, and finally treated on the bed of a reverberatory furnace at a low but gradually increasing temperature for some hours, in admixture with ferrous sulphate. The hearth of the reverberatory, which is of considerable length, is arranged in steps, the mixture of copper oxide and iron sulphate being charged in at the cold end of the furnace and then gently raked forwards towards the hot part near the firebridge. The leaching with hot water and precipitation of the silver is performed as already described, but the residues are differently treated, being next submitted to the *Augustin* process. This process consists in roasting the material containing silver with common salt, much in the manner of the Ziervogel process. The reactions are, however, very different, and in the main consist in the formation of silver chloride either (1) by the direct action of chlorine upon silver, or (2) of hydrochloric acid on silver compounds, or (3) by double decomposition. The roasted charge is then 'leached' with a hot solution of common salt, the silver being precipitated from the solution by sheet copper.

The use of sodium thiosulphate as a solvent for silver chloride was long ago proposed by von Patera, and even employed on a small scale in practice, but it is only within recent years that the 'hyposulphite method' has attained any marked degree of prominence in the treatment of ores. Now, however, it is very largely employed, and owing to the improvement introduced by Mr. Russell, which enables a further percentage of the precious metals to be obtained from the tailings of the ordinary process, this method of treatment bids fair to rival—and even, it may be, in many instances to replace entirely—the ordinary methods of amalgamation.

The Kiss method is a modification in which calcium thiosulphate replaces the sodium salt, the solvent being re-formed by using calcium sulphide as the precipitant, this sulphide being made at the mill by boiling together in water two parts of freshly slaked lime and one part of flowers of sulphur. The duration of the leaching is from ten hours to two or three days. The silver sulphide after precipitation is allowed to settle, the supernatant liquor siphoned off, the precipitate drained on canvas filters, dried, calcined in a reverberatory furnace, fused with litharge and finally expelled.

Both free silver and free gold are partially extracted from the ore by these lixiviation processes, and the writer of this article has received the following description of the ordinary sodium hyposulphite method as practised in Mexico from Mr. H. J. Chaney, A.R.S M.

Mr. Chaney gives two examples, the first of which relates to an ore having the following percentage composition:

SiO_2	Fe_2O_3	MnO	CaO	MgO	S
86·8	2·7	4·25	1·85	2·64	trace.

This ore contained from 25 to 45 ounces of silver per ton of 2,000 lbs.

Roasting and crushing.—It will be seen from the analysis that the above ore was extremely free from base metals and sulphides, the absence of which led to considerable difficulty being experienced in obtaining good results when subjecting it to a chloridising roasting.

In roasting about 8 p.c. of salt was added to the charge, a quantity much larger than would have been necessary had the composition of the ore been more favourable to the process.

As to the method of adding the salt, it was found to be a matter of indifference whether it was added to the ore when it was receiving its preliminary crushing in the stone-crusher, or during the final process of crushing in the battery. It was, however, finally decided to feed the salt into the stone-crusher, whence it passed with the crushed ore by an automatic feed to the 'drier.'

The drier was of the revolving cylinder type (shown in fig. 7), placed at a slight inclination. At one end of this drier is a furnace, the flame from which passes through the drier in an opposite direction to the descending charge. The discharge of dried ore is continuous, but the ore as discharged should be but warm. If too hot the hoppers attached to the battery will be rapidly destroyed.

The stamp battery consisted of twenty-five stamps, each 750 lbs. in weight, crushing dry in twenty-four hours about one ton per stamp. The screen was from 20 to 26 mesh. The size of the screen was of great importance, as the pulp caked to such an extent in the leaching vats that it proved very difficult to deal with. This caking is frequently observed in ore that has been roasted in the Brückner cylinder.

The crushed ore from the battery was carried by endless flanged belts, running beneath the screens, to a receptacle from which it was raised above the roasting furnace by chain elevators, which discharged into hoppers. Each of these hoppers held one roasting charge, 6,500 lbs.

The further treatment of this ore will be considered in conjunction with that of the second ore, the preliminary treatment of which is about to be described. This second ore contained

Pb	Cu	Zn	Fe	SiO_2
6·6	0·2	7·2	1·8	67·5.

It also contained from 40 to 50 ounces of silver per ton of 2,000 lbs.

The metals were present as sulphides. This represents at least the maximum percentage of base metals in an ore, which is permissible if the ore is to be treated economically by ordinary lixiviation. Ores still more 'base' may, however, be treated by the 'Russell process.'

The average weight of this second ore when crushed was about 70 lbs. per cubic foot. The ore was conveyed to the roasters by screw conveyors, the furnaces being fed continuously. The screen which proved most satisfactory was one of 26-mesh. If much coarser the roasting proved unsatisfactory, whilst difficulties were experienced in leaching if a much finer screen was used.

Belt conveyors are much superior to the screw conveyors just mentioned. They are neater in work, and far fewer repairs are necessary.

The stamps used were sixty in number, each 850 lbs. in weight, and crushed about one ton a day per stamp.

The 25-stamp battery treating the ore mentioned in the first example was provided with three Hoffman roasting furnaces. These furnaces differ from the ordinary Brückner furnace in that they have a fireplace at either end. The rotation of the furnace is continued throughout the roasting, at the rate of about three times per minute, the firing being performed alternately at either end. By an arrangement of dampers the flame is caused to traverse the cylinder for its full length. The direction of the flame is reversed every two hours, as the roasting is imperfect at that part of the furnace which is furthest from the fire.

This first ore required from eight to twelve hours to roast completely. It is but rarely that so large a percentage of salt as 8 per cent. is required, but in this instance the chloridisation depended to a great extent on the MnO_2 in the ore, and this occasionally diminished very considerably, the result being an imperfect chloridising action.

Experiments made to prove the influence exerted by the length of time of roasting on the degree of chloridisation of the silver effected gave the following results: After six hours, 62·5 p.c.; after eight hours, 67 p.c.; after ten hours, 85 p.c.; and after twelve hours, 87 p.c. A still more prolonged roasting did not improve the result.

The colour of the roasted ore was a guide to the degree of success of the chloridising action of the salt. Thus a somewhat deep brown colour showed a satisfactory result, whilst a lighter or bluish colour denoted an insufficient roasting.

The success of the roasting depends on the temperature. This should be just sufficient to produce a clotting of the charge, but not to any marked extent. When the roasting furnace has been discharged, the charge is allowed to rest for some time on a cooling floor. During the cooling a distinct chloridising action continues for some time. This amounts usually to an additional 1 or 2 p.c. of the silver present, but it sometimes exceeds 5 p.c., according to the degree to which the roasting was carried, and partly to the nature of the ore treated.

The roasting furnaces at the second mill given as an example, were of the Howell-White type of revolving cylinders. In this furnace there is only one fireplace, the stream of ore and salt gradually falling down the inclined cylinder towards the fire. The cylinder is of iron, and has an internal diameter of about 3 feet, being enlarged near the fireplace in order to admit of a brick lining.

The following are examples showing the percentage of salt added in the roasting of the ore treated at this mill:

Percentage Composition of the Ore				Percentage of Salt added
Pb	Zn	Cu	Fe	
5·00	7·90	0·00	2·14	8·8
6·60	7·20	0·19	1·88	9·3
7·30	9·30	0·22	2·04	9·3
6·80	9·80	0·16	2·34	10·5
8·30	9·10	0·20	2·53	11·0

This, it will be seen, was a very base ore, and its roasting was attended with a considerable loss of silver, the percentage loss being usually at least 5, and sometimes even 10 or 12. This ore was, in fact, much too base for the ordinary lixiviation process, and its treatment was subsequently modified.

The time taken by the stream of ore to pass through the furnace averaged about three minutes. It then fell into vaults, where it remained for several hours. This resulted in a considerably increased degree of chloridisation. As a large quantity of flue dust forms at the point of entrance of the pulp into the furnace, it is necessary to employ an auxiliary fireplace in the flue, which roasts the dust as it is carried forwards by the draught. A large flue with dust chambers is employed.

The temperature of the roasting furnace is not allowed to rise to the point at which the roasting ore will show marked signs of clotting, but it approaches this temperature as nearly as possible.

When it has remained in the vaults for what is found by practice to be a sufficient length of time for chloridisation purposes, it is raked on to a cooling floor, where it is sprinkled with water to prevent the formation of dust during transport.

In one sample of ore treated in this manner it was found that after sprinkling with water the percentage of silver chloride present was considerably diminished. As it was believed that this was due to the presence of lime in the ore, experiments were made to ascertain how this loss might, under such circumstances, be avoided, and the best results were obtained by cooling the roasted ore as rapidly as possible, using a large excess of water.

The ore, having been roasted in the manner described, and the insoluble silver compounds converted into soluble salts, is next submitted to the lixiviation process. After being cooled on the cooling floor by sprinkling with water, it is transferred to waggons on a line of rails above the lixiviation tanks, into which it is then tipped.

Lixiviation.—The lixiviation tanks in the mills described were round ones, each 14 feet in diameter and 3½ feet deep. They were of oak, braced with iron.

Each tank was provided with a false bottom, consisting of a lattice framework covered with coarse sacking. A projecting channel or rim ran around the inside of the tank just above the false bottom, and into this the edge of the sacking was closely packed, to prevent any filtration of ore particles. On this sacking was placed a layer of very coarse gravel six inches in thickness, and above this another six inches of finer gravel, the whole being covered with coarse canvas.

The filter bed thus occupied a space of about a foot in height at the bottom of the tank. Both above and below the level of the filter bed one-inch holes were bored at intervals above one another in the side of the tank. Below the filter bed, too, was an orifice connected with a pipe passing up the outside of the tank.

This arrangement was to allow of the escape of air, which would otherwise stop the filtration. In connection with this, the method of arrangement of the lattice-work is a matter of considerable importance. This must be placed in such a manner that the laths of which it is composed shall point towards the air-hole, it having been found in practice that if placed transversely they will retain air and thus retard the leaching.

The cooled ore, having been charged into tanks such as these, is then carefully 'leached,' water being allowed to enter below the filter bed and to percolate gradually upwards through the ore. When it has reached the surface of the ore in the tank, the supply of water below the filter bed is stopped, and water allowed to flow in at the top of the tank. The plugs fitting into the holes in the tank below the filter are then removed, and the leaching proceeds.

The 'wash water' required will not usually exceed 20 gallons per cubic foot of ore. The effect of this washing is to dissolve out the chlorides of the base metals present in the roasted ore. This solution, or only the first part of it, is run into precipitating tanks, where it is treated with sodium or calcium sulphide.

The precipitation is a partial one, the silver being precipitated as sulphide before the greater portion of the other metals present. When a white precipitate of zinc sulphide begins to be formed, no more sulphide solution is added, as all the silver has then been precipitated. From No. 1 ore, which contained up to about 45 ounces of silver per ton, this sulphide precipitate, after drying and partially burning off the sulphur, was found as the result of a number of monthly averages to contain from 1,800 to 2,000 ounces of silver per ton of 2,000 lbs.

The residues remaining in the tanks after the preliminary washing were even richer in silver than was the ore before washing, so much of the base metals having been removed. Thus the average assays of 1,000 charges of No. 2 ore, each charge amounting to ten tons, showed that while the silver in the unwashed ore amounted to 47·0 ounces per ton, the residue after washing assayed 47·75 ounces per ton.

The preliminary washing of the roasted ore is continued until the wash water no longer yields a precipitate with sodium sulphide. The supply of water is then stopped, and the level of the liquid in the tank allowed to sink until the surface of the ore just shows through it, care being taken to avoid it sinking still lower.

The second stage of the leaching then commences, a solution of sodium hyposulphite being added, and the process of leaching repeated.

In the case of No. 1 ore the hyposulphite solution contained 1 p.c. of the salt, and in that of No. 2 ore 0·75 p.c. In this latter instance experience showed that the weaker, within limits, was the hyposulphite solution, the richer in silver was the sulphide precipitate afterwards obtained, as the following table shows:—

Percentage of hyposulphite in the solution.	Silver in roasted sulphide precipitate, ounces per ton of 2,000 pounds.
0·25	16,380
0·32	17,240
0·35	17,053
0·45	10,471
0·74	7,043

The hyposulphite solution escaping from the bottoms of the leaching tanks, passed to round precipitating tanks, each eight feet deep by five feet in diameter.

In the precipitating tanks either sodium or calcium sulphide is added to the solution for the purpose of precipitating the silver, as in the case of the wash liquor, the solution being agitated while the precipitation is being effected.

After the hyposulphite solution has been turned off, the leaching being considered complete, water is allowed to percolate up through the leached ore to displace the residual hyposulphite solution; and, this done, the leached residues are allowed to fall on an endless flanged india-rubber belt passing below the leaching tubs, and in this way are removed outside the mill, or they are simply removed by shovelling.

In the treatment of an ore assaying 6 p.c. of lead, 7 p.c. of copper, and 40 ounces of silver per ton of 2,000 lbs., the leaching with hyposulphite gave, as the average of a sixteen weeks' mill run, a yield of about 88 p.c. of the silver originally present. During this period 3,320 tons of ore were treated; the leaching of the ore after roasting with salt occupied 1,238 hours, and there were used in this connection 7,386 lbs. of hyposulphite, 47,160 lbs. of lime, and 22,700 lbs. of sulphur, calcium sulphide being used as the precipitant.

The sulphide precipitate containing the silver is roasted on the bed of a reverberatory furnace, the temperature being kept low and the charge stirred continuously. Great difficulty is sometimes experienced, during this roasting, in preventing the loss of silver by volatilisation.

The roasted material is treated in a variety of ways. If relatively poor in silver it may be spread on a bath of molten lead, into which the silver would pass, and from which it could afterwards be separated either by direct cupellation or by any of the other methods described under LEAD. This method involves the loss of a considerable percentage of silver in the form of flue dust, such dust assaying up to 1,000 ounces of silver per ton. If very rich in silver, the precipitate is best treated by being carefully run down in a crucible.

The Russell lixiviation process.—This process depends upon the action of sodium thiosulphate and cupric sulphate upon silver compounds, as in the reactions:

$$1.\ 11Na_2S_2O_3 + 6CuSO_4$$
$$= 2Na_2S_2O_3,3Cu_2S_2O_3 + 6Na_2SO_4 + 3Na_2S_4O_6$$

$$2.\ 2Na_2S_2O_3,3Cu_2S_2O_3 + 3Ag_2S$$
$$= 2Na_2S_2O_3,3Ag_2S_2O_3 + 3Cu_2S.$$

That is to say, the silver sulphide is dissolved by the double salt, copper sulphide being deposited in its stead.

The process is mainly used as an addition to the ordinary process of lixiviation. After the maximum percentage of silver has been extracted by the ordinary lixiviation process, the residues would be then treated by the Russell process. The double copper-sodium salt used as the leaching agent is unfortunately rapidly decomposed when exposed to the action of the air. To avoid this it is customary to make it only at the moment of use. One method of arrangement consists in placing the weighed quantity of sodium hyposulphite and copper sulphate in a box provided with a perforated bottom placed immediately above the ore to be treated. The ordinary hyposulphite leaching solution is allowed to filter through this box before reaching the charge to be leached. The leaching and precipitation are performed in the ordinary manner, as already described. The action of the double hyposulphite is, however, not always rapid, and it may even be necessary to cause the solution to circulate several times through the charge, using an injector pump, or to allow it to remain in contact with the charge during a period of several hours. In a case where an ore rich in the sulphides of lead, copper, zinc, and iron was treated by the Russell process, it was necessary to cause a repeated circulation by the aid of such an injector pump, whilst an ore fairly free from sulphides, but containing much lime, could not be desilverised by such circulation, but only by allowing the solution to remain for some hours in contact with the ore.

The superiority of the Russell process of lixiviation over the ordinary process lies in the fact that while it is an advantage that the silver in the material to be treated should be in the form of chloride or other halogen compound, it is not a necessity, as is the case with the ordinary lixiviation method. An ore, therefore, which has only been imperfectly roasted, or which is chloridised with difficulty, may be desilverised by the Russell process, whilst the lixiviation process proper would not be applicable. This was the case in the following instance:

An ore which had been roasted with salt and then leached with a solution of sodium hyposulphite, was found to retain after such treatment 29·0 ozs. of silver per ton. The Russell process applied to the same roasted ore gave tailings which assayed only 6·9 ozs. per ton. In another case the tailings from the hyposulphite process assayed 48·7 ozs. per ton, and from the Russell process 9·3 ozs.

While, however, the Russell process possesses this advantage as to the increased solubility of the silver, it has one important disadvantage—a large quantity of copper passes into the sulphide precipitate, and this leads to a considerably increased cost of refining. The following are partial analyses of such sulphide precipitates:

Cu	Pb	Fe	Zn	As
19·4	10·5	7·0	10·8	0·25
18·1	6·9	2·0	5·8	0·00

The silver assayed from 8,000 to 10,000 ozs. per ton. The large quantity of lead and zinc present shows that the ore treated was extremely base. It only contained 0·2 per cent. of copper, however; practically the whole of the copper in the precipitate was, therefore, derived from the double hyposulphite used.

Any lead that may be present in the liquor is thrown down by sodium carbonate before the silver is precipitated; any gold that may be in solution passes into the silver precipitate.

The Russell process is in use at the Marsac Mill, Utah (the 'Park Record,' Park City, Utah, Dec. 29, 1888). The plant consists of four ore vats, each 17 feet in diameter and 8½ feet deep, with a capacity of about 65 tons. The precipitating tanks are eight in number; these are 10 feet in diameter and 8 feet deep. Partial precipitation is employed, two tanks being used for the precipitation of the lead by sodium carbonate, four for the precipitation of the silver and gold, and two for the precipitation of the silver from the wash water; sodium sulphide being used as the precipitating agent. Three tanks of the same size as the precipitation tanks are used for the storage of the leaching solution, and there are also the following four rectangular tanks:—

—	Length		Depth		Width	
	Ft.	In.	Ft.	In.	Ft.	In.
I. For storing lead precipitate	17	6	2	9	5	10
II. For storing gold and silver precipitate from leaching	17	4	3	5	4	9
III. Reservoir for leaching solution prior to its being returned by centrifugal pump to storage tanks	17	6	3	5	8	6
IV. For the silver precipitate from the wash water	17	6	3	8	3	5

From the first, second, and fourth of these tanks pipes lead to a pressure-tank, whence the precipitates are forced, by a pressure of 80 lbs. per square inch, to a filter press. After passing this, the precipitate still retains about 50 p.c. of moisture. It is then finally dried, and afterwards desilverised in the manner already described.

The sodium sulphide is prepared by boiling caustic soda and sulphur in a cast-iron tank, 7 feet by 3 feet, and this and the sodium carbonate used for the precipitation of the lead are stored in four wrought-iron tanks, each 7 feet by 3½ feet. In connection with each ore vat is a syphon pump, used in circulating the extra solution.

The cost of this plant was about as follows:—

	Dollars
Labour	6,100
Pipe fittings, castings, and hardware	6,200
Lumber	4,720
Freight, haulage, and general expenses	1,480
Lime, sand, stone, and cement	450
Sundries	50
Total	19,000

The materials used in the treatment of 1 ton of ore are as follows:—

	lbs.
Sodium hyposulphite	1¼
Sodium carbonate	6
Sodium hydrate	5
Sulphur	3⅓
Copper sulphate	5

An analysis of the ore is not given. The cost of treatment per ton of ore is under 6 dollars, as compared with 8·76 dollars in the case of the amalgamation process which was previously employed.

There are numerous other wet methods in use for the treatment of argentiferous ores and products, but they are, for the greater part, merely modifications of those just described. One such process, which possesses considerable importance in the United Kingdom, is the Claudet process. This is adopted in the treatment of the residues obtained from the roasting of the cupriferous iron pyrites, which is imported in large quantities from Spain and Portugal. These residues, in addition to a small percentage of copper, yield rather more than an ounce of silver and a few grains of gold per ton, and this small quantity pays, as a by-product, to extract. The process consists in roasting the material with salt, taking care to obtain the whole of the copper in the cupric form, then leaching with brine, and precipitating the silver with zinc iodide. As the addition of an excess of the precipitant is carefully avoided, any gold present in the solution is precipitated with the silver. After separating and washing this precipitate, it is treated with zinc-dust, in the presence of acidulated water, zinc iodide being re-formed, and the precious metals reduced to the metallic state.

Potassium cyanide may also be mentioned as a solvent for both silver and gold, but its use is accompanied with some difficulty and considerable danger. Much attention has recently been again directed to its use in the treatment of gold ores, and especially of pyrites concentrates. Where the gold is fine, it appears to give good results and is largely used; but it is of no value where the gold is coarse. The precipitation of the gold from the solution—by zinc—is, too, a matter of some difficulty.

Probably the larger proportion of the silver produced annually is obtained by desilverisation of lead; and it has been estimated that, of the quantity of silver produced in 1883, the quantities obtained by the several methods were about as follows:—

Method by which the silver was obtained	Weight of silver produced	Estimated average cost of production of the ounce of fine silver	
	Ounces	*s.*	*d.*
Refining native gold	508,000	0	2½
Desilverisation of lead	30,726,000	2	0
Desilverisation of copper and cupriferous products	7,200,000	1	11
Treatment of silver ores	49,920,733	1	5
Total	88,354,733	——	

The mean average cost, taking the respective weights into consideration, is thus 1*s.* 8*d.* per ounce of fine silver produced.

The United States Mint has since verified the truth of this estimate of the cost of production, considerable doubt as to its accuracy having been expressed (Roberts-Austen, 'An Introduction to the Study of Metallurgy,' London, 1891, p. 286).

The third and fourth methods for the treatment of silver ores—fusion with lead or copper ores—have already been described under Lead and Copper, and a detailed account is therefore unnecessary here. Briefly, the treatment depends, in the case of lead, on the fact that when an ore of silver is brought into contact with metallic lead, or with substances which, under the furnace conditions employed, will yield metallic lead, the silver is reduced from its ore by the lead used, and passes into the excess of that metal. This argentiferous lead is then subjected to some method of desilverisation. Of such methods there are practically but two—one consisting in melting the alloy, allowing it to cool slowly, and then separating the crystals of lead, poor in silver, which have formed in the bath, from the mother-liquor, richer in silver, repeating this operation until a certain limit of richness for the mother liquid has been reached, and then submitting this to an oxidising fusion—cupellation—on a bed of bone-ash or marl. The lead is thus converted into oxide, whilst the silver remains in the metallic form. It will be seen from this description that the process—known, after its inventor, as the 'Pattinson' process—is based on the fact that alloys of lead containing up to a certain percentage of silver—about 2·5—have a lower melting-point than has pure lead.

The second process depends on the fact that, if the lead containing silver and gold is heated above the melting-point of zinc, this metal being stirred in, and the whole allowed to cool slowly, the zinc rising through the molten lead will remove from it both the silver and the gold. As the lead cools the solidified zinc may be removed and the silver and gold recovered from it by some form of distillation process. This results in obtaining a residue of lead rich in the precious metals, which is then cupelled. The lead itself is freed from the residual zinc by subjecting it to an oxidising fusion, or to the action of steam.

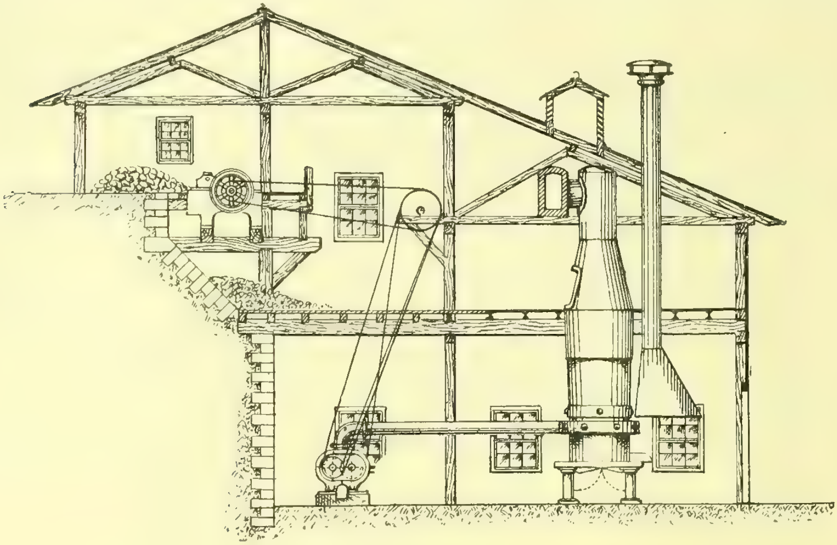


Fig. 13.

The treatment in admixture with ores of lead is effected in Europe chiefly in round blast furnaces; but in out-of-the-way districts where labour is dear, or moulded bricks cannot be obtained, rectangular furnaces are usually employed. This is notably the case in the Western States of America and British Columbia. The general arrangement of such a smelting plant is shown in fig. 13, a light portable cupola replacing the larger form of furnace.

The mode of separating the silver from the lead has been described in the article on that metal (*v.* Lead); but it may be well to point out that in new districts the Pattinson crystallisation process is not applicable owing to the heavy labour cost, the Parkes process of desilverisation of zinc being used instead. Figs. 14 and 15 show the plant in use for the Parkes process at Freiberg, Saxony.

In fig. 14 the lead from a tapping pot (C) runs into the desilverisation pots (A A). These are ordinary Pattinson iron pots. Here it is treated with zinc. The zinc being stirred into the molten lead takes from it any silver and gold that the lead contained. On cooling, the zinc and its contained precious metals may be removed from the surface of the lead bath. Some lead is unavoidably taken over at the same time, and from this the zinc alloy is separated in the liquation pots, B B B. As lead dissolves 1½ p.c. of zinc, and zinc approximately the same amount of lead, as well as silver and gold, both these metals require purification. To free the lead from its contained zinc it is submitted to an oxidising fusion in a reverberatory furnace, D, E representing the main stack of the works. This is an ordinary lead-refining process. The zinc-silver alloy is

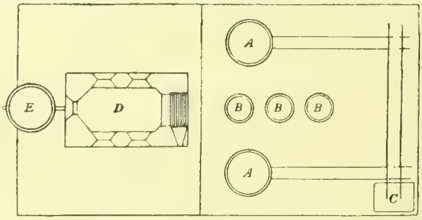


Fig. 14. Parkes' process.

next distilled, the silver, gold, lead, &c., remaining behind while the zinc distils over, is collected, and used again. This distillation is effected at Freiberg in graphite crucibles, A (fig. 15), connected with a condenser (C), and heated in an ordinary wind furnace (B). These crucibles are of the ordinary type, as made by Messrs. Morgan of Battersea.

Various modifications of the Parkes process are in use. In some the zinc is simply stirred into the lead, while in others it is forced below the surface of the lead. Again, the zinc-silver scum, instead of being liquated, may be fused direct with litharge, the zinc being oxidised and the resulting lead cupelled, or after liquation, instead of being retorted in the manner shown in fig. 15, a cylindrical retort may be used, the lead being tapped out directly the zinc ceases to distil over.

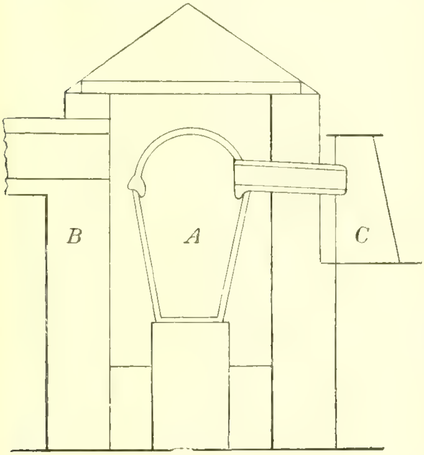


FIG. 15. ZINC DISTILLATION APPARATUS.

When steam, too, is used to dezincify the lead, the lead may be either treated at a red heat for the formation of a zinc oxide—lead oxide scum, which after being raked off, cooled, ground, and washed, can be sold as a paint, or the scum may be treated by the Schnabel process. This consists in treating it in closed iron vessels with a solution of ammonium carbonate, to dissolve out the zinc oxide, then distilling the solution, and by the use of a current of carbonic anhydride regenerating the ammonium carbonate used as a solvent.

The method of procedure adopted after the treatment of ores of silver and gold in admixture with ores of copper, has already been described in connection with the methods of treatment adopted at the works in Colorado and Wales, and need not be further referred to. Sometimes the silver is collected, not in a copper regulus, but in a regulus obtained by fusion with sulphides of iron. Such a regulus would then be treated by one or other of the above methods.

The electrolytic method as used in the desilverisation of copper has already been described in the article on that metal.

The total annual production of silver amounts to approximately 4,000 tons (132,680,000 troy ounces in 1890), and that of gold to about 180 tons. In this connection it is of interest to note that no less than 5,000 tons of silver are in store at the vaults of the United States Treasury at Washington ('Iron Age,' March 26, 1891).

Assaying silver ores.—This is practically identical in principle with the assay of ores of gold, the treatment in both instances consisting in the fusion of the ore to be assayed either with metallic lead or with substances which, under the furnace conditions, yield lead, and a flux. The main difference consists in the much larger percentage of the precious metal in the ore to be assayed.

There are two main methods of assay: (1) crucible methods, and (2) scorification. Wet methods, or mixed wet and dry methods, are of little importance in actual practice.

In crucible methods, if the material to be assayed is a pure siliceous ore, all that is required is to mix it with lead oxide and charcoal, or other reducing agent (flour, sugar, &c.), and some flux, which, with the silica of the ore, will yield a thin fluid slag. Sodium carbonate is best for this purpose where it can be obtained, but such common bases as lime and iron oxide also give satisfactory results. The following mixture and method of assay would be suitable for such an ore: Grind the ore as fine as possible, dry, and determine the moisture. Then weigh out—ore, 300 grains; red lead, 500 grs.; charcoal, 25 grs.; and sodium carbonate, 600 grs. Mix the lead oxide and charcoal intimately together, and then this mixture with the ore to be assayed. This done, mix in one-half of the sodium carbonate, place in a crucible, and heat in a furnace for about 15 minutes at as high a temperature as can be attained without producing a fusion of the charge, the intention being to cause as intimate a contact as is possible between the reduced lead and the silver compounds in the ore, for immediately the charge melts the lead sinks to the bottom of the crucible. The sole hope of collecting the silver from the remaining particles of silver ore, liberated by the solution of the quartz particles in which they were inclosed, then consists in endeavouring to produce a constant current throughout the fused mass, in the hope that in one of its gyrations the silver particle may come into contact with the surface of the lead at the bottom of the crucible. To aid this, the charge is made thin fluid at the end of the first 15 minutes by adding the second half of the carbonate of soda, and then raising the temperature rapidly. At the end of another 10 minutes the mass is poured into an iron mould, the button of lead detached, and the slag re-fused with 300 grains of lead oxide, 15 grs. of charcoal, and 50 or 100 grs. of carbonate of soda. As a matter of fact this precautionary fusion is rarely necessary, provided care is taken to powder the ore very fine, and to pay great attention to the first portion of the crucible assay of the ore—the first 15 minutes.

The lead beads are then cupelled on cupels made preferably of bone-ash, and the resulting button of silver, after having been weighed, and allowance having been made for the silver added with the lead, is parted in the manner described in the articles on ASSAYING and on GOLD. The loss of silver can be determined by a 'check' assay. The following table gives in ozs., dwts., and grs. per ton of 2,240 lbs. the equivalent of the percentages of silver found in the ore by assay :—

Silver or gold per ton of ore				Silver or gold per ton of ore			
Per cent.	=ozs.	dwts.	grs.	Per cent.	=ozs.	dwts.	grs.
0·0001	—	—	15·68	0·0600	19	12	—
0·0002	—	1	7·36	0·0700	22	17	8
0·0010	—	6	12·8	0·0800	26	2	16
0·0020	—	13	1·6	0·0900	29	8	—
0·0030	—	19	14·4	0·1000	32	13	8
0·0040	1	6	3·2	0·2000	65	6	16
0·0050	1	12	16	0·3000	98	—	—
0·0060	1	19	4·8	0·4000	130	13	8
0·0070	2	5	17·6	0·5000	163	6	16
0·0080	2	12	6·4	0·6000	196	—	—
0·0090	2	18	19·2	0·7000	228	13	8
0·0100	3	5	8	0·8000	261	6	16
0·0200	6	10	16	0·9000	294	—	—
0·0300	9	16	—	1·0000	326	13	8
0·0400	13	1	8	2·0000	653	6	16
0·0500	16	6	16	3·0000	980	—	—

If the ore contains much sulphur it should be submitted to a preliminary roasting, the carbon added to the charge should be slightly increased, and a piece of hoop-iron, or large nails, &c., should be added, for the purpose of decomposing any lead sulphide which might otherwise be produced. Instead of roasting, an addition of nitre may be made.

If the ore to be examined contains much copper it is best to add an iron sulphide, such as pyrites, for the purpose of causing the copper to collect in the form of a regulus; much of it would otherwise pass into the lead. In this case, too, metallic iron should be used in the assay, and the slag and regulus should be re-treated.

In 'scorification' methods the ore is mixed with granulated metallic lead, and then raised to a high temperature. A small shallow dish, called a 'scorifier,' is used for this purpose, and the process consists in submitting the fused mixture to the action of an oxidising atmosphere. The lead oxide which forms acts as a flux for the siliceous gangue and other impurities of the ore, and the silver is retained by the excess of lead remaining unoxidised, from which it may be regained by cupellation as before.

In practice this method is as follows: Mix, say, 50 grs. of the ore with 250 grs. of granulated lead, and place the mixture in the carefully-dried scorifier. Then cover over with another 250 grs. of lead, and sprinkle 5 grs. of borax over the surface. This done, place the scorifier in a moderately hot muffle, and raise the temperature gradually to a dull-yellow heat. A ring of litharge will form round the edge of the scorifier, and will gradually extend inwards, until the whole of the lead has been covered. This lead oxide will retain some silver; it is therefore desirable to scatter a small quantity of carbon (3 to 5 grs.) over the surface of the molten oxide. The result is to reduce a portion to the metallic state, and the reduced lead, forming at the surface, in its passage through the litharge exerts a desilverising action on it. Let the scorifier remain in the muffle until the 'eye' has again disappeared—until the litharge surface has re-formed—and then remove, pour, and detach the lead bead. If soft, this may be cupelled; but if hard, from the presence of impurities, it must be rescorified before cupellation.

The dry assay of silver in this manner admits of very great accuracy. Telluride ores are, however, somewhat difficult to deal with, owing to their volatility. To such an extent is this the case that it may be necessary in assaying an ore of this character by the scorification method, to use, not 10 times the weight of lead, as given above, but 50, or, it may be, even 100, times the weight of the ore. Such ores are, however, rare. For the assay of bullion *v.* art. ASSAYING.

Alloys.—Almost the only important alloys of silver are the alloys of silver with copper used for coinage. In 1,000 parts of such alloys the silver contained is either 400, 500, 600, 700, 720, 750, 800, 810, 830, 833·3, 835, 868, 900, 902·7, 905, 916·66, 917, 925, or 945, the standard of the United Kingdom being 925, that of the Latin Union 900 and 835, and of the Scandinavian Union 800, 600, and 400 (*v.* ALLOYS).

Literature.—Among the more important treatises and papers relating to the metallurgy of silver are the following:—G. Küstel, 'Roasting of Gold and Silver Ores,' San Francisco, 1880; Bruno Kerl, 'Grundriss der Metallhüttenkunde,' Leipzig, 1880; C. A. M. Balling, 'Die Metallhüttenkunde,' Berlin, 1885; Phillips-Bauerman, 'Elements of Metallurgy,' London, 1887; T. Egleston, 'Metallurgy of Silver, Gold, and Mercury,' vol. i. London, 1887; C. A. Stetefeldt, 'The Lixiviation of Silver Ores,' New York, 1888; A. Arche, 'Die gewinnung der Metalle,' Leipzig, 1888, &c.; M. Eissler, 'The Metallurgy of Silver,' London, 1889; Royal Commission on the cost of production of the precious metals, Report, 1887; E. Fremy, Encyclopédie Chimique, 1889, 'Silver,' by R. de Fourcrand, and 'Gold,' 1888, by E. Cumenge and E. Fuchs; L. Knab, 'Traité de Metallurgie,' Paris, 1891; C. Schnabel, 'Lehrbuch der Allgemeinen Hüttenkunde,' Berlin, 1890.

There are also numerous important papers and statements relating to the treatment of silver ores in the Transactions of the American Institute of Mining Engineers and in the Official Reports of the United States Mint, and Mining Commissioner. E. J. B.

Silver, allotropic or colloidal. Carey Lea (Am. S. 1889, vol. i. p. 476, vol. ii. pp. 47, 129, 237; 1891, vol. i. p. 482, vol. ii. p. 312) finds that by the action of certain reducing agents upon silver solutions the metal may be obtained as a dark-coloured precipitate, which if brushed on paper, glass, &c., dries with its particles in optical contact. The colours of the silver are brilliant, so that the golden-coloured variety dried on paper resembles gold leaf. Perfect mirrors are produced if glass is used.

The reducing reagents may be metallic salts of organic acids, such as a mixture of ferrous sulphate and sodium citrate, or ferrous sulphate and Rochelle salt. Or metallic compounds may be avoided, and an alkaline solution of brown dextrine or of tannin employed.

On analysis, the samples prepared by means of iron salts yield, after drying *in vacuo* over sulphuric acid, 97–98 p.c. of silver (in one case nearly 99 p.c.), the remainder being oxide of iron and organic acid, with sometimes a little water. The dextrine preparation may contain from 3 to 8 p.c., or even more, of organic matter not removable by washing.

Some preparations are soluble in water, giving a solution that is yellow, deep red, or black, according to its concentration. Such solutions are precipitated by neutral substances in general, alkaline nitrates, sulphates or citrates giving a precipitate that dissolves in water after washing, while magnesium sulphate and many other salts precipitate an insoluble form.

Allotropic silver has been obtained of many colours, such as ruby-red, blue-green, reddish-brown, and one form is a dark bronze colour when wet, and like burnished gold, or copper-coloured, when dry. All forms of the solid are brittle and easily powdered when dry, they easily amalgamate with mercury, and are instantly converted by acids, even when dilute, to grey normal silver with absolutely no evolution of gas. The halogens and such compounds as sodium hypochlorite and ferric chloride give magnificent colours, blue predominating, due to thin films. Platinic, stannic, and auric chlorides give no colour reactions. Some samples are changed to grey normal silver by *friction* (such as the shaking of loose pieces in a bottle during a railway journey, or by drawing a glass rod over the surface), or by *exposure to light*.

A form of silver intermediate between ‘allotropic’ and normal silver is golden yellow, and has a high lustre, but has none of the other properties of allotropic silver. It is produced by heating allotropic silver, but not sufficiently to change it into normal grey silver (*v.* also Barus and Schneider, Zeits. f. phys. chem. 8, 278; Schneider, B. 1891, 3370).

SILVER ASSAYING *v.* ASSAYING.

SILVER OXIDES AND SALTS. Three oxides are said to exist, the suboxide Ag_4O (?) (*v. Silver sub-salts* &c.), the protoxide or normal oxide Ag_2O, and the peroxide Ag_2O_2(?).

Silver protoxide Ag_2O, generally known as silver oxide, is obtained as a brown, hydrated precipitate by addition of potash to silver nitrate, or as a bluish-black powder by boiling the precipitated chloride with concentrated potash. According to Carnelley and Walker (C. J. 1888, 79), the hydrated oxide is unaffected by a temperature of 100°, but from that temperature to 180°, it rapidly loses water and a little oxygen, with formation of the anhydrous oxide and some metallic silver. Above 270° it rapidly loses its oxygen, which is entirely evolved at about 300° to 340°.

According to Bruce (C. N. 50, 208), the hydroxide obtained by mixing dilute solutions of silver nitrate and potash in alcohol of 90 per cent. at −50°Fah., is almost white. It, however, soon darkens, and is brownish even at −40°Fah.

Silver oxide dissolves in ammonia, and is soluble in water to the extent of 1 part in 3,000 (Bineau, C. R. 41, 509), the solution having an alkaline reaction and a metallic taste. Acids dissolve it, with production of salts, which are generally anhydrous. The recently precipitated moist oxide absorbs carbon dioxide from the air (Rose, P. 85, 304). Hydrogen reduces silver oxide to metal at 100°. Tin and copper also reduce it in presence of water.

When the freshly precipitated oxide is dissolved in ammonia and the solution exposed to the air, the *fulminating silver* of Berthollet (Crell's Annalen, 1788, 2, 390) separates out as a black powdery precipitate or in black lustrous crystals. When dried, it explodes violently on the slightest friction; in fact, explosion frequently occurs under water. Acids convert it into ammonia and silver salts. According to Raschig (A. 233, 93), it has the composition NAg_3.

Silver oxide is used to impart a yellow colour to glass. It frequently replaces the nitrate in medicine, as its discolouring action on the skin after prolonged internal use is much less (*v.* U.S. Dispensatory, 14th ed. 1093).

Silver peroxide. The body to which this name is usually applied was first obtained by Ritter by the electrolysis of a silver nitrate solution. According to Berthelot (C. R. 90, 653), it separates on the cathode on electrolysis of a 10 per cent. solution in large, thick, black, striated, lamellar needles of brilliant metallic lustre. The crystals fall to a black amorphous powder, with evolution of some oxygen, on exposure to the air. A little above 100° the peroxide gives off oxygen with explosion. It dissolves in concentrated sulphuric acid to a green liquid, which evolves oxygen, with precipitation of the normal silver sulphate on dilution. Ammonia decomposes it, with evolution of nitrogen and formation of silver protoxide.

The composition of this body is not known. Wallquist (J. pr. 31, 179) ascribes the formula Ag_2O_2, but Fischer (J. pr. 32, 108) finds less oxygen than that formula requires, and Berthelot (C. R. 90, 653) ascribes to it the composition $4Ag_2O_3 2AgNO_3 H_2O$. It may, however, be prepared from the sulphate, and then in general properties resembles the compound obtained from the nitrate, though not distinctly crystalline. When prepared from the nitrate, it always contains that substance, which can only be partly removed by prolonged washing. A peroxide of the composition Ag_2O_2 is also said to be obtained by the action of ozone on silver, and Berthelot (C. R. 90, 572) states that the action of hydroxyl on silver protoxide results in a mixture of silver and an oxide of the composition Ag_2O_3.

Silver carbonate Ag_2CO_3 is obtained by precipitating silver nitrate with an alkaline carbonate, as a white precipitate, which turns yellow on washing and is blackened by light. It is said to lose the whole of its carbon dioxide at 200°. A solution of the salt in ammonia gives, on addition of alcohol, a grey precipitate having the composition $Ag_2CO_3 4NH_3$.

According to G. S. Johnson (C. N. 54, 75), it is obtained in crystals by dissolving the precipitated carbonate in water saturated with carbon dioxide at 15°. He has also obtained it in large glistening yellow prisms, which melt at low redness, and decompose at a somewhat higher temperature, with evolution of carbon dioxide, by exposure of the oxide in presence of water to the air for two months. Schulten (C. R. 105, 811) has obtained a white precipitate which changes to microscopic crystals of the composition $AgKCO_3$, by the addition of silver nitrate to a concentrated solution of potassium carbonate containing free carbon dioxide. Water decomposes the crystals, with formation of the normal carbonate.

Silver nitrate $AgNO_3$, is usually prepared by dissolving silver in nitric acid, and is largely so obtained in the 'parting' of silver from gold by nitric acid (*v.* art. Gold, 2, 266). The salt may be freed from copper by boiling with freshly precipitated silver oxide, which precipitates the copper as oxide, or by heating the fused salt until the copper nitrate has been decomposed, which occurs before the silver salt is affected. When a portion dissolved in water and treated with ammonia gives no blue colour, the mass is cooled, dissolved in water, filtered from the copper oxide, and recrystallised. In working up photographic and other silver residues, the chloride produced from solutions by addition of hydrochloric acid, and the ash of papers, &c., is mixed with four or five times its weight of sodium carbonate or of a mixture of potassium and sodium carbonates, and is heated in a crucible to bright redness, when the silver collects as a button in the bottom of the crucible. The precipitated chloride may also be reduced by zinc or iron in water slightly acidulated with hydrochloric or sulphuric acid.

Silver nitrate crystallises in colourless rhombic tables of sp.gr. 4·328 (Schröder, P. 106, 226), melting at 218° (Carnelley, C. J. 1878, 276), and resolidifying to a fibrous crystalline mass. When the fused salt is cast in sticks, it forms the *lunar caustic* of pharmacy. At a heat much below redness, it is decomposed into silver nitrite, with evolution of oxygen, and at a red heat into silver, nitrogen peroxide, oxygen, and nitrogen.

Water dissolves the nitrate with formation of a neutral solution; hot alcohol dissolves about a fourth of its weight; strong nitric acid has but little solvent action. According to Kremers (P. 92, 497), its solubility in 100 parts of water is:—

0°	19·5°	54°	85°	110°
121·9	227·3	500	714	1111

Tilden and Shenstone (Tr. 175, 33) find that 100 parts of water at 125° dissolve 1622·5 parts, and at 133° no less than 1941·4 parts of the salt.

Dry silver nitrate absorbs ammonia, with evolution of sufficient heat to fuse it, and production of a compound of the formula $AgNO_33NH_3$ (Rose, P. 20, 153). Ammonia nitrates of the composition $AgNO_3NH_3$ (Reychler, B. 16, 992, and 2421) and $AgNO_3.2NH_3$ (Mitscherlich, P. 9, 413; Kane, A. Ch. 72, 288; and Marignac, Ann. M. [5] 15, 25), have also been prepared. Double nitrates of the composition $AgNO_3KNO_3$, $AgNO_3RbNO_3$, and $AgNO_3AmNO_3$ are described by Ditte (C. R. 101, 878), who, however, fails to obtain the compounds $AgNO_32NaNO_3$ and $AgNO_34NaNO_3$ described by Rose.

Senderens (C. R. 104, 175, and 504) has examined the action of zinc, lead, tin, and aluminium, and of selenium, tellurium, arsenic, phosphorus, iodine, and bromine on aqueous silver nitrate.

Silver nitrate is used as a marking-ink and as a constituent of certain hair dyes, and is very largely employed in photography. It is used in medicine both externally and internally (*v.* Squire's Companion to the British Pharmacopœia, 1890, 79, and the U.S. Dispensatory, 1879, 1,088).

Silver nitrite $AgNO_2$ is best obtained by precipitating silver nitrate solution with potassium nitrite (V. Meyer, A. 171, 23). It forms a white crystalline powder, difficultly soluble in cold water. From hot solution it separates in yellowish needles or prisms. It melts at about 134° with partial decomposition (Divers, C. J. 24, 91).

Silver sulphate Ag_2SO_4 may be obtained by dissolving the metal in concentrated sulphuric acid or by dissolving the oxide or carbonate in the acid. It dissolves easily in sulphuric or nitric acid, but requires about 200 parts of cold or 68·58 parts of hot water for solution (Kremers, P. 92, 499).

Silver sulphate crystallises in small rhombic prisms isomorphous with anhydrous sodium sulphate (Mitscherlich, P. 12, 138), and fusing at 654° (Carnelley, C. J. 1878, 279).

An acid salt $HAgSO_4$ crystallising in pale-yellow prisms, and a double sulphate with aluminium (silver alum) $Ag_2Al_24SO_424H_2O$ (Church, C. N. 9, 155) are also known. The latter salt crystallises in octahedra, which are decomposed by water into the component sulphates.

Silver sulphite Ag_2SO_3 is obtained in small, white glistening needles, or as a white curdy precipitate, by dissolving silver oxide in sulphurous acid and crystallising, or by precipitating a silver salt with sulphurous acid or a sulphite. Heat readily decomposes it into silver, silver sulphate, and silver sulphite. Several double alkaline sulphites are known.

Silver thiosulphate or hyposulphite $Ag_2S_2O_3$ is obtained as a snow-white, slightly soluble powder, of sweetish taste, by addition of dilute silver nitrate to excess of concentrated sodium thiosulphate (*v.* Herschel, Edin. Phil. J. 1, 26 and 2, 154). It forms two series of double salts with the alkali metals of the composition $RAgS_2O_3$ and $R_4Ag_2S_6O_9$. The salt $NaAgS_2O_3$ is obtained by evaporating a solution of silver chloride in sodium thiosulphate. The ammoniacal solution of this salt may be used for silvering. Cohen (C. J. 1887, 39) describes a thiosulphate of the composition $Ag_2S_2O_3.2K_2S_2O_3$.

Silver chromate Ag_2CrO_4 is obtained in dark-red crystals by the addition of potassium chromate solution to silver nitrate. It dissolves in alkaline chromates and in the nitrates of ammonia and the alkalis (R. F. Carpenter, S. C. I. 5, 286, and Biscaro, C. N. 53, 67). By cooling a hot ammoniacal solution of silver chromate yellow crystals of $Ag_2CrO_44NH_3$ are obtained.

Silver chromate has been employed in miniature painting.

Silver bichromate $Ag_2Cr_2O_7$ is obtained in dark, reddish-brown, triclinic prisms, somewhat soluble in water, by precipitating potassium bichromate with silver nitrate.

Silver phosphates. Several phosphates are known. The normal orthophosphate Ag_3PO_4 is obtained as a lemon-yellow powder, insoluble in water, but readily soluble in acids and ammonia, by precipitating a silver nitrate solution with an orthophosphate. Joly (C. R. 103, 1071) has obtained it in rhombic dodecahedra. It fuses at about 849° (Carnelley, C. J. 1878, 280). The diargentic phosphate Ag_2HPO_4 may be obtained in colourless hexagonal prisms (Joly, *l.c.*), which become yellow in contact with water or alcohol, with decomposition into the normal salt and phosphoric acid. Silver pyrophosphate $Ag_4P_2O_7$ is obtained as a white precipitate by addition of sodium pyrophosphate to silver nitrate. It fuses at 585° (Carnelley, *l.c.*) to a brown liquid, which re-solidifies to a white mass of radiating crystals. It is soluble in ammonia, from which it is precipitated unchanged by acids. The metaphosphate $Ag_2P_2O_6$ or $AgPO_3$ is obtained as a crystalline powder, slightly soluble in water, and fusing at 482° (Carnelley, *l.c.*) to a transparent glass, by precipitating silver nitrate with sodium metaphosphate.

Silver tartrate $Ag_2C_4H_4O_6$ is obtained as a white curdy precipitate on mixing solutions of Rochelle salt and silver nitrate. It is nearly insoluble in water, but dissolves in dilute ammonia. This solution deposits its silver as a shining mirror when gently heated, and under various modifications, and is largely employed in silvering glass. A good mixture is prepared as follows: (1) Dissolve 5 grams of silver nitrate in 100 c.c. of distilled water and add ammonia until the precipitate first produced is nearly dissolved. (2) Dissolve 1 gram of silver nitrate in 20 c.c. of water, heat to 110°F., and add a solution of 0·83 gram of Rochelle salt in 10 c.c. of water. Boil the mixture for ten minutes, filter, and dilute to 500 c.c. The glass, after washing with potash, dilute nitric acid, and alcohol, rinsing after the application of each, is covered with a mixture of equal volumes of these solutions at about 80°F. After an hour, the silver will have deposited in a coherent film, which may be polished or varnished after a few days (*v.* Cooley's 'Cyc. of Practical Receipts,' 1872, 1,044; Varley, 'Year-book of Photography,' 1890, 114).

W. H. Perkin (C. J. 1887, 362) describes an acid tartrate $C_4H_5AgO_6H_2O$ crystallising in large brilliant monoclinic prisms, from a mixture of strong silver nitrate and tartaric acid solutions.

Silver fumarate $C_4H_2Ag_2O_4$ is precipitated as a white amorphous powder, requiring over 200,000 parts of water from solution, by addition of the acid or its salt to a solution of silver nitrate. It explodes on heating. Warnerke ('Year-book of Photography,' 1876, 131) has proposed its use in photography.

Silver fulminate *v.* article FULMINIC ACID, vol. ii. p. 166.

Silver sulphide Ag_2S occurs native in *argentite, vitreous silver*, or *silver glance*. As double sulphide, it occurs in red silver ore $3Ag_2S.Sb_2S_3$. It may be obtained by heating silver chloride in a current of sulphuretted hydrogen, by heating silver with sulphur or sulphuretted hydrogen, or by precipitating silver solutions with sulphuretted hydrogen.

Silver sulphide is sufficiently soft to be cut with a knife. It fuses readily without change, but when roasted in the air becomes gradually converted into silver. It is decomposed by boiling strong sulphuric, nitric, and hydrochloric acid, and is converted into the chloride by digestion with cuprous chloride solution. The presence of sodium chloride facilitates the latter reaction, which is employed for removing silver from certain ores by dissolving the silver chloride as fast as formed.

Silver sub-sulphide *v. Silver sub-salts &c.*

Silver selenide Ag_2Se is a dark-grey body, which melts at a red heat to a silvery mass. It is obtained by heating silver with selenium, or by precipitating a silver solution with seleniuretted hydrogen. A di-selenide Ag_2Se_2 is also known. Selenides of silver and lead (*naumannite*) and of silver and copper (*eukarite*) occur in nature.

Silver chlorides. Two chlorides are said to exist, the normal salt AgCl and the sub-chloride Ag_2Cl (?). Peculiar compounds which appear to be combinations of the normal and sub-chloride, and which are known as photochlorides, are also known. Regarding them and the sub-chloride, and the action of light on silver salts *v. Silver sub-salts &c.*

The normal silver chloride occurs in *horn silver* or *cerargyrite*, and as the double chloride and bromide of silver in *embolite*. It is obtained by the action of chlorine or hydrochloric acid gas on silver, or as a dense, curdy, white precipitate, which gradually becomes powdery, by addition of hydrochloric acid or a soluble chloride to silver nitrate solution. Silver chloride assumes a yellow colour when heated, and melts at 451° (Carnelley, C. J. 33, 278). It solidifies to a soft, tough, horny mass, having a sp.gr. of 5·594 (Schröder, P. 106, 226). According to Kohlrausch (W. 17, 642), the electric conductivity of silver chloride exceeds that of the bromide or iodide, and when fused exceeds that of sulphuric acid.

The fused chloride is not appreciably soluble in cold water, though very slightly soluble in hot (Stas, C. R. 73, 998). The precipitated chloride is more soluble, and the washings become cloudy on addition of either hydrochloric acid or silver nitrate. In concentrated hydrochloric acid its solubility is about 1 in 200, and in the acid diluted with its own volume of water 1 in 600. It is much more soluble in alkaline chlorides, especially sodium chloride, and dissolves readily in ammonia. Pure strong nitric acid at 15° to 17° dissolves the precipitated chloride to the extent of 2·01 parts in 100,000 (Thorpe, C. J. 25, 453). Soluble thiosulphates and sulphites, and ferric chloride also dissolve it, and potassium cyanide converts it into a soluble double cyanide AgCN.KCN, together with potassium chloride. It dissolves readily in coniine (Blyth, C. J. 1, 350) and in solution of methylamine (Wurtz, A. Ch. [3] 30, 453). Silver chloride is slowly decomposed by boiling concentrated sulphuric acid (Sauer, Fr. 1873, 376).

Silver chloride is not reduced by carbon, but may be reduced by fusion with four or five times its weight of sodium carbonate, or of a mixture of sodium and potassium carbonates. Iron, zinc, and other oxidisable metals reduce it in presence of water, especially when acidulated with hydrochloric or sulphuric acid.

Digestion with potassium bromide or iodide solution decomposes the chloride with formation of potassium chloride and silver bromide or iodide (Field, C. J. 10, 236). The chloride is converted into the bromide or iodide when fused in a current of air containing bromine or iodine vapour (Julius, C. N. 48, 284). It may be partly converted into the bromide by digestion with bromine water (*v.* Humpidge, B. 17, 1838; Potilitzin, J. Russ. Chem. Soc. 1882, 82, and B. 17, 1308; Berthelot, C. R. 94, 1619).

Silver chloride, bromide, or iodide, precipitated from solution containing a colouring matter such as an aniline dye, has a characteristic colour which cannot be removed by washing. The compounds produced by the different haloid salts with the same dye frequently differ considerably in colour. Somewhat similar compounds are obtained when silver chloride is precipitated from a solution containing a metallic salt, such as the chloride of iron, cobalt, nickel, manganese, copper, or gold (Carey Lea, Am. S. 34, 384).

Dry precipitated silver chloride rapidly absorbs large volumes of ammonia gas, which it again gives off at 37·7° (Faraday, Quarterly J. of Sc. 5, 74). According to Rose (P. 20, 157), the amount absorbed corresponds with the formula $2AgCl.3NH_3$.

Silver chloride formed a constituent of the sensitising material used in the original platinotype process (Willis, Photographic J. 1891, 123).

Silver bromide AgBr occurs native as *bromargyrite*. It is obtained by addition of a soluble bromide to silver nitrate, as a yellowish, curdy precipitate, less soluble in ammonia than the chloride, but more so than the iodide. In dilute ammonia it is almost insoluble. It dissolves in hot hydrobromic acid or mercuric nitrate solution, and crystallises out in octahedra. It is also soluble in potassium and other bromides, forming double salts, and in sodium thiosulphate. According to H. W. Vogel (B. 16, 1170, and 18, 861; *v.* also Eder, B. 18, 1256, and De Pitteurs, Chem. Centr. 1884, 411), two molecular modifications of silver bromide exist, the one precipitated from aqueous solution, and the other from solution in alcohol of at least 96°. The former is said to be most sensitive to certain of the blue rays, and the latter to certain of the indigo rays.

Silver bromide fuses to a reddish liquid at 427° (Carnelley, C. J. 33, 277). Its sp.gr., after fusion, is given by Schröder (P. 106, 243) as 6·349, that of the precipitated bromide being 6·418. The electric conductivity of silver bromide is less than that of the chloride, but exceeds that of the iodide. When fused it conducts better than sulphuric acid (Kohlrausch, W. 17, 642).

Gaseous hydrochloric acid decomposes it at 700° with evolution of hydrobromic acid. Chlorine decomposes the freshly precipitated bromide.

According to Rammelsberg (P. 55, 248), the dry bromide absorbs no ammonia; but it separates from ammoniacal solution in crystals containing ammonia, which is driven off by heat (Liebig, Schweigger's J. für Chem. und Phys. 48, 103).

Carey Lea describes peculiar compounds produced by precipitating silver bromide in presence of various colouring matters and metallic salts (*v. Silver chlorides*).

Regarding the sub- and photobromide, and the action of light on silver bromide *v. Silver sub-salts &c.*

Silver iodide AgI occurs naturally as *iodargyrite* or *iodyrite*. It may be obtained by heating silver with iodine, by dissolving silver in hydriodic acid, or by precipitating silver nitrate with a soluble iodide.

Silver iodide is of a pale primrose colour, and is insoluble in most acids, and almost insoluble in ammonia, but dissolves in potassium iodide and soluble thiosulphates. It dissolves in hot hydriodic acid, and separates on cooling in colourless flaky crystals of the composition AgI.HI (*v.* Deville, C. R. 32, 894). It is decomposed by hot concentrated nitric or sulphuric acid with evolution of iodine. When gently heated in chlorine, or when heated to 700° in hydrochloric acid gas, it is converted into the chloride.

Silver iodide absorbs ammonia gas with formation of a white compound, of the composition $2AgI.NH_3$, which evolves ammonia on exposure to the air (Rammelsberg, P. 48, 170).

When precipitated by excess of potassium iodide, silver iodide is unaffected by light, but it is rendered sensitive by the presence of a trace of silver nitrate, chloride, or bromide, which converts the last trace of potassium iodide into the silver salt (*v.* Abney, Pr. 33, 164).

The abnormal expansion and contraction of the iodide when heated was first noticed by Fizeau (C. R. 64, 304), and has since been examined by Deville (C. R. 64, 323), Mallard and Le Chatelier (C. R. 97, 102), and Bellati and Romanese (Pr. 34, 104); and more fully by Rodwell (Pr. 33, 97; 25, 280; 31, 291). When heated it acquires a brilliant yellow colour and passes through various shades of orange, until, at 527° (Carnelley, C. J. 33, 278), it fuses to an orange-red liquid. On cooling the fused iodide, it contracts considerably at the solidifying-point, and continues to contract, until, at 116°, it expands suddenly and violently, and passes from the amorphous to the crystalline form. The iodide appears to exist in three modifications: (1) as a plastic, tenacious, amorphous, reddish, transparent substance between 116° and its melting-point; (2) as a brittle, opaque, crystalline mass below 116°; (3) as a yellow, brittle, amorphous mass, obtained by pouring the fused iodide into cold water.

The determinations of the specific gravity of the iodide vary considerably. According to Deville (C. R. 64, 323), the sp.gr. of the fused iodide at 0° is 5·687, that of the precipitated iodide being 5·807 at 0°. According to Kohlrausch (W. 17, 642), the electric conductivity of silver iodide is less than that of the bromide or iodide, but the conductivity of the fused salt exceeds that of sulphuric acid.

Carey Lea describes peculiar compounds produced by precipitating silver iodide in presence of various colouring matters and metallic salts (*v. Silver chlorides*).

Regarding silver sub-iodide and photoiodides *v. Silver sub-salts &c.*

Silver fluoride, AgF, may be obtained as a deliquescent, very soluble salt, by dissolving silver oxide in hydrofluoric acid. It crystallises from solution in quadratic pyramids, of the composition $AgFH_2O$ (Marignac, J. 1856, 129), or in prisms of the composition $AgF2H_2O$ (Frémy, J. 1856, 87; Pfaundler, J. 1862, 86). The hydrated salt loses water when dried *in vacuo*. Most of the water is driven off, together with some oxygen and hydrofluoric acid, when heated in a covered vessel to the melting-point of lead. After expulsion of all the water, the fluoride may be heated to the melting-point of silver without change. The dry salt absorbs 844 times its volume of ammonia.

When a solution of the fluoride is strongly concentrated over the water-bath, or when the crystallised hydrated fluoride is dried over sulphuric acid, brass-yellow spangles, of the composition AgF.AgHO, are obtained (Pfaundler, J. 1862, 87; *v.* further, Gore, Tr. 1869, 191, 192; 1870, 227; 1871, 321).

Silver sub-fluoride *v. Silver sub-salts* &c.

Silver cyanide AgCN is obtained as a white, curdy precipitate by addition of a soluble cyanide to silver nitrate solution. It dissolves readily in ammonia and soluble cyanides, and slightly in hot dilute nitric acid, but not in the cold acid or in water. Sulphuric or hydrochloric acid decomposes it with evolution of hydrocyanic acid.

The ammoniacal solution contains the compound $AgCN.NH_3$, while the cyanide solutions contain double cyanides, such as AgCN.KCN; AgCN.NaCN; 3AgCN.2KCN.NaCN (Baup, A. Ch. [3] 53, 462). The double cyanide of silver with a heavy metal is best obtained by addition of silver potassium cyanide to a solution of a salt of the metal. Silver potassium cyanide, which is employed in the electroplating bath (*v.* art. ELECTROPLATING, ii. 2), crystallises in regular octahedra, soluble in 4 parts of water at 20°, and in 25 parts of alcohol of 85 p.c. at 20° (Baup, *l.c.*).

Silver cyanate AgCNO is a white, somewhat soluble powder, which explodes on heating. It may be obtained by the addition of silver nitrate to potassium cyanate solution.

SILVER SUB-SALTS, PHOTOSALTS, AND SUB-OXIDE; ACTION OF LIGHT ON THE HALOID SALTS.

The existence of a suboxide of silver Ag_4O was first affirmed by Wöhler (A. 30, 1), who stated that when silver citrate is heated to 100° in a current of hydrogen, it is reduced to a sub-citrate and free citric acid, 1 atom of oxygen passing off as water. The residue dissolves in water to a brown solution, from which a black precipitate of the reputed suboxide is deposited on addition of potash. Wöhler's work has been repeated by Von Bibra (J. pr. 1875, 12, 39), Bailey and Fowler (C. J. 1887, 416), Newbury (Am. 8, 196), and Muthmann (B. 20, 983). According to Bailey and Fowler, carbon dioxide is given off as well as water, except at the very earliest stages of the reduction, and the solution of the resultant body gives the reactions of itaconic acid and shows no argentous citrate. Newbury, however, while also noticing the evolution of carbon dioxide, and failing to obtain a sub-oxide, states that the red solution is turbid from the presence of finely-divided silver, and contains much free citric acid. Bailey and Fowler also failed to confirm Faraday's statement (A. Ch. 9, 107), that a sub-oxide, Ag_4O_3, is obtained by exposure of a solution of silver oxide in ammonia to the air.

O. v. der Pfordten (B. 20, 1458; 3375) obtained a black compound, which he first described as the suboxide Ag_4O, but to which he subsequently gave the formula Ag_4H_2O (B. 21, 2288), by the following process: 20 c.c. of a 12·5 p.c. solution of sodium tartrate was mixed with a solution of 2 grms. of silver nitrate in $1\frac{1}{3}$ litres of water, adding 2 c.c. of a 4 p.c. solution of soda, and stirring violently. After 5 hours the liquid was decanted, and the residual black precipitate of argentous tartrate (?) was washed with dilute sodium sulphate and treated with alkali, which converted it into the above compound. The same substance was obtained by the action of alkali on the black precipitate obtained by the gradual addition of 4 c.c. of concentrated phosphorous acid solution to a solution of 10 grms. of silver nitrate in 20 c.c. of water, to which sufficient ammonia had been added to re-dissolve the precipitate at first produced. The body thus obtained is a deep black amorphous powder, which is decomposed by water, and requires to be kept under alkali. It is insoluble in ammonia or acetic acid, and is decomposed, with separation of metal, by hydrochloric, sulphuric, and most other acids, but is not affected in the cold by sulphurous or phosphorous acid. Hydroxyl has no action in the cold, but reduces it to silver when warmed; mercury fails to remove any silver. When acted on by sulphuretted hydrogen, it produces black amorphous sulphide, which becomes grey when dried, and which is slowly decomposed by water. It dissolves in potassium cyanide and in warm dilute nitric and hydrochloric acids, water precipitating it unchanged from the latter. Strong nitric and sulphuric acids decompose it with separation of sulphur.

Bailey (C. N. 55, 263) and Friedheim (B. 20, 2554; 21, 307) dispute these results, the latter stating that the so-called argentous hydrate is a mixture of silver, with more or less argentic oxide and organic matter. Geuther (A. Ch. Pharm. 114, 121) states that the suboxide is obtained by the action of precipitated cuprous oxide on silver nitrate; and, according to Güntz (see below), it is obtained by the action of steam on the sub-fluoride at 160°, but he gives no analysis of the product.

For the preparation of the sub-chloride, to which the formulæ Ag_2Cl (Wöhler) and Ag_4Cl_3 (Von Bibra) have been applied, several methods have been proposed. Wöhler (A. 30, 3) states that it is obtained as a black powder, which is decomposed by ammonia into silver chloride and silver, by the action of hydrochloric acid on argentous citrate prepared as above. Wetzlar (Schweigger's J. für Chem. und Phys. 1828, 2, 466) affirms its production by the action of cuprous or ferric chloride on silver. Von Bibra (J. pr. 1875, 12, 39) and Newbury (Am. 8, 196) fail to obtain it by either Wöhler's or Wetzlar's process. A very complete bibliography on the sub-salts of silver is given by Von Bibra (*l.c.*).

Güntz (C. R. 110, 1337; 112 (1891), 861) prepared a fluoride of the composition Ag_2F by electrolysis of a saturated solution of the normal fluoride with a powerful current, using silver electrodes, and allowing the liquid to become hot. It is then obtained on the cathode in brass-coloured plates, which are unaffected by dry air, but are rapidly decomposed by water, with precipitation of silver and production of silver fluoride. The same compound is said to be produced when finely-divided silver is heated in a sealed tube, at a temperature below 90°, with silver fluoride solution. Compare Pfaundler (*Silver fluoride*).

According to Güntz, the sub-fluoride is converted into the violet *sub-chloride* when dry hydrochloric acid, or, better, the vapour of the chloride of carbon, silicon, or phosphorus, is passed over it. Analysis of the sub-chloride indicates the presence of some normal chloride. Gaseous hydriodic acid similarly gives a *sub-iodide* Ag_2I, with considerable rise of temperature. Sulphuretted hydrogen produces the *sub-sulphide* Ag_4S; and steam passed over the sub-fluoride heated to 160° produces the sub-oxide.

Carey Lea (Am. S. 33, 349, 480, 489; 34, 33) has produced an important series of coloured haloid salts of silver, to which he has given the name 'photosalts,' and which he regards as identical with the so-called sub-salts forming the latent photographic image. They appear to be compounds of the normal and sub-salts, the proportion of halogen in the chlorides corresponding to from under 1 p.c. to over 8 p.c. of the sub-chloride; in the iodide, corresponding to from 0·64 to 4·63 p.c.; and in the bromide sometimes corresponding to as much as 7 p.c. of the sub-salt.

The photochloride, which the bromine and iodine compounds resemble in general properties and methods of preparation, may be obtained in various colours, varying through salmon, pale pink, rose, copper-red, reddish purple, chocolate, and other shades, to black.

The following are some of the methods of preparation: (1) the chlorination of the metal; (2) the partial reduction of the normal chloride; (3) the reduction of silver oxide or carbonate by heat, with subsequent treatment by hydrochloric acid; (4) the treatment of the sub-oxide or a sub-salt with hydrochloric acid, followed by nitric acid; (5) the treatment of the sub-chloride with nitric acid or an alkaline hypochlorite; (6) the treatment of a solution of silver nitrate with ferrous, manganous, or chromous oxide, and treatment of the product with hydrochloric acid; (7) the treatment by hydrochloric acid of the product of the reduction of silver citrate in hydrogen; (8) treatment of a silver solution with potash or soda and a reducing agent, such as milk sugar, or any easily oxidisable body, the precipitate being treated with hydrochloric acid.

These salts are permanent in the dark, but become purple or purplish-black when exposed to light. They are all decomposed by strong nitric acid, and slowly dissolve in ammonia, ammonium chloride, and sodium chloride, leaving a little silver. When heated, the photosalts are altered in colour, usually towards redness. Thus the grey salt may become pink at 100°, while the dark varieties may turn chocolate-coloured or purple at that temperature.

The action of light on the chloride, and similarly on the bromide and iodide, has been variously attributed to the production of metal, sub-chloride, and oxy-chloride; and, more recently, by Carey Lea (*l.c.*; *v.* also C. Staats, B. 21, 2199), to the formation of a photochloride.

The evolution of chlorine under the action of light is indisputable, but the composition of the residue is still doubtful. S. B. Newbury (Am. 6, 407) and others consider it to be a mixture of the normal chloride and silver, and Tommasi (Bl. [2] 37, 291) considers that the product in the case of silver bromide consists of the unchanged salt with a sub-bromide and metallic silver. Hitchcock (Am. 11, 474) found as much as 4·2 to 4·9 p.c. of chlorine eliminated from thin films of silver chloride exposed to sunlight in a *current of hydrogen.* Carey Lea (Am. S. 38, 356) has shown that anhydrous silver chloride or iodide is darkened by light under petroleum, where the production of any quantity of oxychloride is impossible. Richardson has made a similar experiment with carbon tetrachloride (C. J. 1891, 544).

See further regarding the action of light on the halogen salts, Abney (Pr. 33, 164; 40, 251), Staats (B. 20, 2322), Griveaux (C. R. 107, 837), Richardson (C. J. 1891, 536); and regarding the action of dyes in modifying the sensitiveness of silver to different parts of the spectrum (orthochromatic photography) *v.* H. W. Vogel (B. 6, 1302; W. 26, 527), Eder (Sitz. B. 1884, 1117; M. 6, 1 and 7, 1), and Bothamley (S. C. I. 1887, 423; Brit. J. of Photography, 35, 499).

SILVERING is the art of covering the surface of bodies with a thin film of silver. This is now effected either by applying thin films of silver mechanically to the article to be silvered, or by the electro-metallurgical process. When silver leaf is to be applied, the methods prescribed for gold leaf are suitable. Among the metals, copper or brass are those on which the silverer most commonly operates. Iron is seldom silvered, but the processes for both metals are essentially the same. The white alloy of nickel is now often plated.

The principal steps of this operation are the following:—

1. The *smoothing down* the sharp edges, and polishing the surface of the copper; called *émorfiler* by the French artists.

2. The *annealing*; or making the pieces to be silvered red hot, and then plunging them in a very dilute nitric acid till they are bright and clean.

3. *Pumicing*; or clearing up the surface with pumice-stone and water.

4. The *warming*, to such a degree merely as when it touches water it may make a slight hissing sound; in which state it is dipped in the very weak aquafortis, whereby it acquires minute insensible asperities, sufficient to retain the silver leaves that are to be applied.

5. The *hatching*. When these small asperities are inadequate for giving due solidity to the silvering, the plane surfaces must be hatched all over with a graving tool, but the chased surfaces need not be touched.

6. The *blueing* consists in heating the piece till its copper or brass colour changes to blue. In heating, they are placed in hot tools made of iron, called *mandrins* in France.

7. The *charging*; the workman's term for silvering. This operation consists in placing the silver leaves on the heated piece, and fixing them to its surface by burnishers of steel of various forms. The workman begins by applying the leaves double. Should any part darken in the heating, it must be cleared up by the scratch-brush.

The silverer always works two pieces at once, so that he may heat the one while burnishing the other. After applying two silver leaves, he must heat up the piece to the same degree as at first, and he then fixes on with the burnisher four additional leaves of silver, and he goes on charging in the same way, four or six leaves at at time, till he has applied, one over another, 30, 40, 50, or 60 leaves, according to the desired solidity of the silvering. He then burnishes down with great pressure and address till he has given the surface a uniform silvery aspect.

Silvering by the precipitated silver chloride. The white curd, obtained by adding a solution of common salt to one of silver nitrate, is to be well washed and dried. 1 part of this powder is to be mixed with 3 parts of good pearlash, 1 of washed whiting, and 1½ of sea salt. After cleaning the surface of the brass it is to be rubbed with a bit of soft leather, or cork moistened with water and dipped in the above powder. After the silvering it should be thoroughly washed with water, dried, and immediately varnished. Some use a mixture of 1 part of the silver precipitate with 10 of cream of tartar, and this mixture also answers very well.

Others give a coating of silver by applying with friction, in the moistened state, a mixture of 1 part of silver powder precipitated by copper, 2 parts of cream of tartar, and as much common salt. The piece must be immediately washed in tepid water very faintly alkalised, then in slightly warm pure water, and finally wiped dry before the fire. The inferior kinds of plated buttons get their silvery coating in the following way:—

Two ounces of silver chloride are mixed up with one ounce of corrosive sublimate, 3 pounds of common salt, and 3 pounds of zinc sulphate with water into a paste. The buttons, being cleaned, are smeared over with that mixture and exposed to a moderate degree of heat, which is eventually raised nearly to redness, so as to expel the mercury from the amalgam formed by the reaction of the horn silver and the corrosive sublimate. The copper button thus acquires a silvery surface, which is brightened by cleaning and burnishing (Ure, 3, 834).

SILVER WHITE. *Blanc d'argent* v. Pigments.

SIMILOR. A rich-coloured brass, said to be composed of three ounces of zinc to one pound of copper.

SINALBIN $C_{30}H_{44}N_2S_2O_{16}$, a crystalline substance contained in white mustard seed (*Sinapis alba*), of a sharp taste, easily soluble in water, and converted by myrosin into sinalbin mustard oil, acid sulphate of sinapine and glucose.

SINAPINE *v.* Vegeto-alkaloids.

SINAPOLINE *Diallyl urea* $CO(NH.C_3H_5)_2$. A crystalline substance obtained by boiling mustard oil with baryta water or lead oxide.

SINODOR. A term for a basic magnesium acetate (*v.* Acetic acid; also Magnesium).

SINTZ. A name applied to incrustations on rocks or elsewhere, from mineral waters. According to the nature of the deposit, it is distinguished as calcareous sintz (calcspar or arragonite), siliceous (quartz or opal), ferruginous (fitticite), arsenical (scorodite), &c. (Watts).

SKATOLS *v.* Indoles.

SKUTTERUDITE. *Triarsenide of cobalt v.* Cobalt.

SLATE. (*Ardoise*, Fr.; *Schiefer*, Ger.) A fine-grained sedimentary rock, usually argillaceous, characterised by a highly fissile structure. The fissility, termed *slaty cleavage*, is due to a rearrangement of the particles of the rock consequent on compression, and it has been shown by Sorby and others that the direction of cleavage is at right angles to that in which the pressure was applied; hence the planes of cleavage need not bear any relation to the original bedding of the rock. For an able discussion of the subject of slaty cleavage *v.* A. Harker, in Rep. Br. Ass. for 1885, 813.

Most slates have originally been clayey sediments, and they consequently present much the same chemical composition as clays. It is notable that minute acicular crystals of rutile are often abundant. (On the origin of slate and of the rutile *v.* W. M. Hutchings, Geol. Mag. 1890, 264, 316; 1891, 164, 304, 459.) Many secondary minerals, such as chiastolite and staurolite, may be developed in slate, especially where it is invaded by igneous rocks, such minerals being commonly found in the zone of metamorphism around granite intruded into an area of slate.

The best slates occur in North Wales, where they have been worked since at least the sixteenth century. The principal quarries are those of Penrhyn, near Bangor, and Dinorwig, near Llanberis, where purple and green slates are worked in the Llanberis group of the Cambrian system. The slates quarried around Ffestiniog occur at a higher geological horizon, being referable to the Llandeilo beds. In Cornwall and Devon, slaty rocks of Devonian age are abundantly developed, and have been extensively quarried at Delabole and Tintagel in North Cornwall.

Slates are not only valued as roofing material, but are used in large slabs for cisterns, flags, steps, tombstones, billiard tables, &c. Mantelpieces are often constructed of slate, and enamelled to imitate marble or serpentine. Minor uses of slate are for splitting into school slates and cutting up into slate pencils. For pencils a soft fine-grained material is required, but as only small pieces are used there is no disadvantage in the rock being broken up by joints and cleavage-planes. The Skiddaw slate of the Lake District is used for pencils. The green slates of the Borrowdale series of Cumberland, which are used for roofing, consist chiefly of fine volcanic ash, in which perfect cleavage has been developed by compression.

Although the term 'slate' should properly be restricted to rocks which exhibit superinduced cleavage, it is often extended to fissile rocks which split along the original planes of bedding. Such thin flaggy rocks occur in the Oolitic system, and though not so thin and light as true slates, are used for sake of their picturesque effect, especially in Gothic buildings. The *Stonesfield slates* of Oxfordshire, and the *Collyweston slates* of Rutland are calcareous sandstones of this character. Such slates are not readily split into thin slabs when first quarried, but need exposure to a winter's frost in order to develop their latent fissility.

(For the details of quarrying and dressing slate *v.* D. C. Davies, Slate and Slate Quarrying, London, 1878.) F. W. R.

SMALT *v.* Cobalt.

SMALTINE. *Cobalt arsenide v.* Cobalt.

SMILACIN *v.* Sarsparilla.

SMITHSONITE *v.* Zinc.

SOAP. The term 'soap,' in the widest sense, includes a large number of metallic salts derived from one or other of the numerous body of 'fatty acids,' the glycerides or glycerin salts of which are the main constituents of the various naturally occurring oils and fats of the animal and vegetable kingdoms. Comparatively few of these salts, however, are employed for any useful purpose outside of the laboratory, those chiefly prepared being lead soaps, as ingredients in certain kinds of pharmaceutical plaisters; lime, magnesium, and zinc soaps, formed in the treatment of certain oils and fats by particular processes employed in preparing materials for candle-making; and potassium and sodium soaps, which constitute the main ingredients in the numerous class of ordinary household, laundry, and manufacturing soaps, to which, in ordinary use, the term 'soap' is usually restricted. The manufacture of these articles essentially consists in the treatment of oily and fatty matters with the alkalis potash and soda, in more or less pure condition, in such a fashion as to bring about the change called, in consequence, *saponification*—viz. the conversion of the natural glycerin salt contained in the fatty matter into the corresponding alkali-metal salt, with elimination of glycerin, the change being expressible in the case of the glyceride *tristearin*, the leading constituent of tallow, by the equation

$$\underset{\substack{\text{Glyceryl tri-stearate,}\\ \text{890 parts.}}}{\left.\begin{matrix}C_3H_5\\(C_{18}H_{35}O)_3\end{matrix}\right\}O_3} + \underset{\substack{\text{Caustic soda,}\\ \text{120 parts.}}}{3\left.\begin{matrix}Na\\H\end{matrix}\right\}O}$$

$$= \underset{\substack{\text{Glycerin,}\\ \text{92 parts.}}}{\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3} + \underset{\substack{\text{Sodium stearate,}\\ \text{918 parts.}}}{3\left.\begin{matrix}Na\\C_{18}H_{35}O\end{matrix}\right\}O},$$

and by parallel equations in other cases; the general character of the chemical change being one of double decomposition, the alkali-metal of the alkali used exchanging places with the organic radicle of the glycerin, so as to form a potash (or soda) salt of the fatty acid instead of a glycerin salt. Under certain conditions alkaline carbonates can be substituted for caustic alkalis, carbonic acid being then liberated during the reaction; as a rule, higher temperatures (obtainable under increased pressure) are requisite to effect this change. Some considerable amount of soap, moreover, is at the present day prepared by separating, by one or other of several methods, from natural fats and oils the fatty acids therein contained as glycerides, and subjecting the product to pressure, so as to squeeze out the more liquid portions, leaving behind the acids of higher melting-point, which are employed for candle-making &c.; the more fluid 'oleines' (as the liquid or semi-solid fatty acids are generally, but erroneously, called) are then directly neutralised with alkali so as to form soaps by combination, just as any other salt is obtainable by putting together the appropriate acid and base; thus

$$\underset{\text{Oleic acid.}}{\left.\begin{matrix}C_{18}H_{33}O\\H\end{matrix}\right\}O} + \underset{\text{Caustic soda.}}{\left.\begin{matrix}Na\\H\end{matrix}\right\}O} = \underset{\text{Sodium oleate.}}{\left.\begin{matrix}C_{18}H_{33}O\\Na\end{matrix}\right\}O} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}.$$

The number of natural vegetable oils and butters (semi-solid oils) capable of undergoing saponification, and thereby furnishing more or less useful soaps, is very large and continually increasing, through the exploration of new countries and districts and the bringing into commerce of novel natural products therefrom; but the oils actually used in large quantities, and in which any considerable trade is done otherwise than simply locally, are comparatively few in number, the leading ones being palm, palmnut, cocoanut, olive, cotton-seed, groundnut, sunflower, sesamé, linseed, rape, hemp, poppy, niger, castor, and sweet almond-oils; also shea butter and analogous semi-solid oils, and so-called 'vegetable tallows.' Of the animal fats and oils the most important are tallow, lard, and suet, and the analogous 'kitchen grease' and fat from horses and other dead animals not used for food; various trade refuses, *e.g.* from skin dressing, tanning, &c., and especially bone-boiling and glue-making; whale, sperm, and seal oils, and cod and various other fish oils. Few substances of oleaginous or greasy nature, however, come amiss to the soapmaker, so that the 'foots' of oil refiners (masses of albuminous and similar vegetable substances separated during refining by means of acids and alkalis, and retaining considerable amounts of fatty matters intermixed) are highly valuable materials; whilst the extraction by means of benzene, carbon disulphide, petroleum spirit, and other analogous solvents of fatty substances contained in oil cakes unfit for feeding purposes, the marcs and crushed residues of oleiferous seeds, and even engine waste (greasy rags used for cleaning machinery, &c.), constitutes a very considerable trade; and the separation of grease from soapsuds used in cleansing woollen and other textile fabrics, and even the scum from sewage, can often be profitably conducted on account of the possibility of using the recovered grease for the manufacture of the coarser kinds of soap. The yolks of eggs, the whites of which are largely used for albumin in calico printing, and the natural greasy matters obtained from sheep's wool (suint), similarly contain a sufficient amount of saponifiable constituents to render them capable of being employed for the preparation of certain forms of impure soap.

The principal fatty acids derivable from the most frequently employed oils and fats belong to one or other of four well-marked families, indicated respectively by the formulæ noted in the table on next page.

As regards the alkalis used in soap-making it may be noticed that formerly potashes from land vegetation, and kelp and barilla from the incineration of marine vegetation, and of *salsola soda*, were the substances mainly employed; in these the alkalis existed as carbonates, and, in order to render them available for saponification, *causticising* was essential, effected by boiling with lime in not too concentrated a solution, so

Name	Formula	Melting point	Chief sources
	Stearic family $C_nH_{2n}O_2$.		
Lauric acid . .	$C_{12}H_{24}O_2$	44°C.	Cocoanut oil; laurel butter (bay fat)
Myristic acid . .	$C_{14}H_{28}O_2$	54°	Nutmeg butter; also in cocoanut oil and spermaceti
Palmitic acid . .	$C_{16}H_{32}O_2$	62°	Palm oil, and to some extent in most animal fats
Stearic acid . .	$C_{18}H_{36}O_2$	69°	Tallow, lard, suet, and the chief animal fats; olive oil, almond oil
Arachidic acid . .	$C_{20}H_{40}O_2$	75°	Earthnut oil
Benic acid . .	$C_{22}H_{44}O_2$	76°	Oil of ben
	Oleic family $C_nH_{2n-2}O_2$.		
Physetoleic acid .	$C_{16}H_{30}O_2$	30°	Sperm oil
Hypogæic acid .	$C_{16}H_{30}O_2$	34°	Earthnut oil
Oleic acid . .	$C_{18}H_{34}O_2$	14°	Most animal fats, especially the softer ones; olive oil
Erucic acid . .	$C_{22}H_{42}O_2$	33-34°	Colza oil
	Linoleic family $C_nH_{2n-4}O_2$.		
Linoleic acid . .	*$C_{18}H_{32}O_2$	—	Linseed oil
	Ricinoleic family $C_nH_{2n-2}O_3$.		
Ricinoleic acid .	$C_{18}H_{34}O_3$	—	Castor oil
Rapic acid . .	$C_{18}H_{34}O_3$	—	Rape seed oil

* Formerly regarded as $C_{16}H_{28}O_2$, but shown by recent researches to be indicated by the higher formula here assigned.

that the carbonates became hydroxides in virtue of the reaction (in the case of soda)

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

When the artificial production of soda from salt by Leblanc's process (involving the two stages of conversion into sulphate by treatment with sulphuric acid, and heating the 'salt-cake' thus produced with limestone or chalk and small coal) became general, soapmakers frequently made their own alkali direct from salt; latterly, however, the preparation of soda in this way, as also the similar transformation of mineral potassium chloride into caustic potash, and the still later ammonia process for converting common salt into carbonate of soda by treatment of brine with ammonia and carbonic acid gas, have gradually become more or less dissevered from soap-making proper; so that at the present day a very large proportion of the soap of commerce is prepared from carbonated alkalis manufactured outside the soap works, and only requiring causticising before use; whilst there is an increasing demand for solid caustic alkalis packed in drums for export and smaller users, so as to avoid the necessity of putting up causticising plant. For further details of the manufacture of the alkaline carbonates and hydroxides *v.* articles POTASSIUM and SODIUM.

It is obvious that the nature of the fatty matter to be operated upon will greatly modify the proportions subsisting between the fatty matter saponified, the alkali required to decompose it, and the soap resulting from the operation. Of the leading substances used in soap-making, tallow requires, for a given weight, the least alkali to produce complete saponification, and forms the smallest quantity of soap, whilst cocoanut oil requires the most alkali, and produces the largest proportion of soap: tallow, consisting of the glycerides tristearin and triolein, $\left.\begin{matrix}C_3H_5\\(C_{18}H_{35}O)_3\end{matrix}\right\}O_3$ and $\left.\begin{matrix}C_3H_5\\(C_{18}H_{33}O)_3\end{matrix}\right\}O_3$, of molecular weights 890 and 884 respectively, whilst cocoanut oil has a mean composition corresponding approximately with that of trilaurin $\left.\begin{matrix}C_3H_5\\(C_{12}H_{23}O)_3\end{matrix}\right\}O_3$, molecular weight 638. 1,000 parts of tallow consequently would require from $\frac{1000}{890} \times 120$ to $\frac{1000}{884} \times 120$—*i.e.* from 123·6 to 124·4 of caustic soda NaOH for saponification, and would furnish $\frac{1000}{890} \times 918$ to $\frac{1000}{884}$ 912—*i.e.* from 1031·5 to 1031·6 parts of sodium stearate and oleate; whilst 1000 parts of cocoanut oil would require $\frac{1000}{638} \times 120 = 188{\cdot}1$ parts of caustic soda, and would furnish $\frac{1000}{638} \times 666 = 1043{\cdot}9$ parts of sodium laurate.

In a general way the soaps obtained with potash as alkali are far softer than the corresponding soda soaps, the precise texture in any given case being largely dependent on the nature of the fatty acids present, and the quantity of water, excess of alkali, and saline matters, &c., incorporated with the final product. What are termed *soft soaps*, accordingly, mainly contain potash as alkali; whilst the 'hard' soaps of commerce (ordinary scouring, household, and laundry soaps) usually contain only soda. Many of these are increased in detergent power by intermixing with the soap proper, during the course of manufacture, such substances as aluminate of soda, silicate of soda, and the alkaline compound obtained by treating resin with soda, or are 'hardened' and rendered firmer in texture and less readily dissolved or softened by similarly incorporating neutral salts (such as sodium sulphate) so as to prevent waste during use. It by no means follows that because an oil is soft or semi-solid, therefore a firm solid soap cannot be obtained from it, although this is sometimes the case—*e.g.* with certain fish oils. Thus cocoanut oil yields a soda soap so comparatively hard in texture (especially in presence of silicate of soda or other hardening salts) that larger quantities of water can be incorporated therewith without destroying its solidity than with almost any other known kind of soap. Similarly the 'oleine' of the candle maker can be made to furnish a perfectly solid 'hard' soda soap, especially when a certain amount of excess of alkaline matter is also present; as also do horse grease and other soft animal fats when the resulting soap is intermixed with a little sodium sulphate. On the other hand, typical 'soft' soaps are obtained by saponifying drying oils, such as linseed and poppyseed oils, with potash, the softness of texture being to some extent increased through the non-separation from the resulting soap of the complementary glycerine.

Most soaps are fairly soluble in pure water; but the presence of more than certain small limiting quantities of saline matter in the water entirely prevents solution, so that on adding such salts to an aqueous solution of soap, the soap is rendered insoluble, and separates from the aqueous liquor.[1] This circumstance is taken advantage of in the process of manufacture as a means of purification, ordinary kitchen salt or excess of alkaline ley being the material usually chosen as separating agent. When solutions of potash soaps are thus 'salted out' with chloride of sodium the two alkalis usually change places, so that a soda soap separates out whilst potassium chloride remains in solution. This method of preparing soda soaps, using potashes as the primary saponifying agent, was formerly of considerable industrial importance, especially in districts where soda was scarce, and the ashes of wood and vegetation abundant. It is noticeable that the opposite change can be to some extent brought about under proper conditions. Thus, if a pure soda soap be dissolved in water, and a considerable amount of potassium chloride added to the solution, the separated soap consists of a mixture of soda and potash soaps in proportions varying with the nature of the soap and the relative masses of potassium and sodium present, the potash soap sometimes predominating. If fatty acids be neutralised by means of a mixture of equivalent quantities of potash and soda used in excess, both alkalis become converted into soap in sensibly equal proportions, and not one of them to the more or less complete exclusion of the other; whilst on boiling a soda soap with potash ley, or a potash soap with soda ley, mixed potash and soda soaps result, the two alkalis forming soaps in practically the proportions in which they are present in the total mass. On the other hand, when potassium carbonate is added to a molten moist soda soap double decomposition takes place, potash soap and sodium carbonate being formed, whilst but little reaction ensues between sodium carbonate and molten potash soap under similar conditions. These different behaviours are apparently due to the circumstance that potash, although but a slightly stronger base than soda, has nevertheless a markedly greater tendency to unite with the stronger acid present when two acids are there simultaneously; so that in the case of soaps in contact with alkaline chlorides, the prevailing tendency is towards the formation of potassium chloride, and the combination of soda with the weaker organic fatty acid (this tendency being somewhat modified according to the relative masses of sodium and potassium present); whilst in the case of soaps in contact with alkaline carbonates, the leading tendency is towards the formation of potash soap, the weaker carbonic acid associating itself with the soda in preference (*v.* Alder Wright and Thompson, S. C. I. Nov. 1885). The improvement in texture produced by 'pearlashing' certain kinds of soda soap (adding a certain proportion of pearlash dissolved in a little water to the molten soap) in the manufacture of toilet soaps has long been known, although the exact *modus operandi* of the pearlash has only recently been cleared up, and shown to be the formation of softer potash soap, along with sodium carbonate equivalent to the pearlash used.

Hydrolysis of soap.—During actual use the value of soap, as a detergent agent, is largely due to the fact that contact with water breaks up a neutral soap into one containing more acid than one equivalent for one of alkali present, the alkali corresponding to the excess of acid becoming free, and consequently enabling water to come thoroughly into contact with, and to properly wet, the substances washed, even though coated with faint films of greasy matter, or other substances exerting capillary repulsion for water. The actual amount of hydrolytic action thus brought about in any given case varies with the nature of the fatty acids, being greater *cæteris paribus* with soaps made with cottonseed and cocoanut oils, and less with sodium stearate, than with castor oil soap or sodium palmitate or oleate. In all cases it increases with the proportion of water relatively to the soap. With acids of the same family, the higher the molecular weight the less apparently is the hydrolytic action of a given proportion of water upon a pure soap. The action also is slackened if the water contains alkaline matter in addition to the soap; or, what amounts to the same thing, if the soap contain excess of alkali over and above that requisite to saturate the fatty acids present. Alcohol, it may be noted, unless dilute, produces no decomposition at all of a neutral soap. The following table exhibits the results of a variety of experiments upon the rate of hydrolysis of different kinds of soap (Alder Wright, Cantor Lectures, Journ. Soc. Arts, vol. xxxiii. 1885), the figures representing the percentages of alkali, originally present as neutral soap, that became free on treating one part of soap with *M* parts of water :—

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[1] Cocoanut and palm kernel soaps are far more soluble in saline fluids than most other soaps, whence their use for 'marine soap,' which will lather with sea-water.

Soaps prepared from	Hydrolysis brought about by M parts of water					
	$M=10$	$M=15$	$M=25$	$M=50$	$M=100$	$M=150$
Pure stearic acid	0·75	1·0	1·5	2·4	3·4	3·8
Nearly pure palmitic acid	1·5	1·8	2·3	3·0	3·5	3·9
Crude lauric acid (cocoanut oil soap)	3·5	4·0	4·7	5·7	6·75	7·0
Pure oleic acid	2·1	2·6	3·5	4·75	6·3	7·1
Crude ricinoleic acid (castor oil soap)	1·75	2·25	2·75	3·6	4·3	4·6
Palmitic, stearic, and oleic acids in nearly equal proportions (palm oil and tallow soap)	1·2	1·5	2·25	3·75	5·0	5·6
Tallow-resin soap (primrose)	1·7	2·2	2·9	4·0	5·0	5·6
Cottonseed oil soap	2·25	2·8	4·2	6·5	9·0	9·8

Manufacture of soap.—The exact period when the knowledge of the art of soap-making was first acquired is somewhat uncertain. True soap does not appear to have been known to the early Jews and Greeks; but an imperfect product, prepared from goat's tallow and wood-ash lye, is described by Pliny, whilst the ruins of a fairly well-appointed soap factory have been unearthed at Pompeii. The use of lime for causticising alkaline liquors, and the softer texture of soap prepared from wood-ash alkali (potash), as compared with barilla (soda), were probably only imperfectly, if at all, understood at this epoch; whilst, as regards the actual chemistry of the soap-making process, our knowledge is of entirely modern origin, being first gained by the researches of Chevreul. At the present day numerous methods and modifications and varieties of processes are in use to a greater or lesser extent for the preparation of soaps of various kinds. These may be conveniently classified in five groups, viz.:—

Group I. Processes in which free fatty (and resinous) acids are directly neutralised with alkalis. For this purpose the alkalis need not necessarily be causticised with lime, but may often be employed as carbonates. Glycerin is obviously not produced during the formation of the soap, and is not contained in the finished article.

Group II. Processes in which fatty glycerides are treated with alkalis (usually previously causticised) so as to saponify them, forming soap and setting free glycerin, these two products not being separated from another subsequently, so that the finished soap is mixed with glycerin.

Group III. Processes in which soap and glycerin are formed from fatty matters and alkalis, and are then separated from one another, so that the soap finally produced contains little or no admixed glycerin.

Group IV. Processes consisting of combinations of various methods of the preceding types.

Group V. Processes through which soaps, prepared by some or other of the foregoing methods, are subsequently put for special reasons; such as remelting and blending, scenting, and shaping into tablets, &c., for toilet purposes; intermixture with other materials, such as water for purposes of adulteration, antiseptics for sanitary purposes, silicate or carbonate of soda to cheapen and increase detergence, or refining and de-alkalising materials to remove excess of alkali and render less corrosive to tender skins; solution in alcohol to render transparent, &c.

Group I. The methods of the first class are in practice only applied to the 'oleine' of the candle-maker, and similar recovered greases consisting of free fatty acids, and for the production of 'resinate' of soda for intermixture with boiled soaps prepared in other ways in the manufacture of certain kinds of yellow soap. When carbonated alkali is used to neutralise the free fatty acids a vigorous effervescence ensues owing to the escape of carbon dioxide gas; in consequence, a 'curb' is provided at the top of the mixing pan, consisting of a kind of funnel or wide hoop, temporarily affixed to obviate loss by frothing over. Caustic alkali, however, is for several reasons more convenient than carbonate, whilst the extra cost is but small, so that its use is ordinarily preferred. The manufacture in this case is carried out in the simplest possible fashion. A steam-jacketed pan is provided furnished with an efficient agitator, one of the best forms of which consists of two sets of vertical vanes moving in opposite directions so as to interlace in passing. The 'red oil' or 'oleine' is run into the pan and heated up by means of the steam jacket; the proper quantity of alkaline ley, usually previously heated in a separate pan, is then run in, and the whole thoroughly intermixed by means of the agitator, after which the mass is transferred to a 'cooling frame,' in which it gradually solidifies to a solid block of soap. The amount of alkali used is best gauged by employing a properly graduated tank, and running in a known volume of fluid of accurately known strength. For every 282 parts of oleic acid 40 of caustic soda, NaOH, are theoretically required; a slight excess is ordinarily employed, part of which separates out as a fluid exudation during the solidification of the block, whilst the rest remains disseminated through the mass, rendering it more or less rich in 'free alkali'—*i.e.* excess of uncombined alkaline matter. According to the percentage of water intended to be present in the finished soap the strength of the ley varies; thus, if to 282 parts of oleic acid 140 of ley be added containing 45 of caustic soda, the resulting soap will contain 304 parts of anhydrous soap,[1] and 5 excess of caustic soda; so that neglecting loss by exudation, evaporation, &c., the finished soap will contain 113 parts of water, or 27·3 per cent.; with, of course, proportionately more water if a weaker ley be used (containing the same amount of soda) and *vice versâ.* In practice the strength of the alkaline ley is usually known with sufficient exactness from its sp.gr. found by means of a hydrometer. It is to be noticed, however, that as ordinary commercial soda ash and caustic soda always contain more or less neutral salts (sulphate, chloride, &c.), the quantity of actual alkali present in a given ley is always appreciably smaller than that deduced from the sp.gr. determination, the deficiency being greater the larger the proportion of saline impurities present.

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[1] 282 parts of acid and 40 of soda forming 18 of water and 304 of anhydrous soap, in virtue of the reaction $C_{18}H_{34}O_2 + NaOH = H_2O + C_{18}H_{33}NaO_2$.

Some makers work up 'red oils' into soap in a slightly different way, boiling up the oils with weak leys, and salting out the partly formed soap in much the same way as that adopted in the preparation of soaps by processes of Group III. (*v. infra*); when this method is adopted, more or less grease or other glycerides are usually worked up with the red oils, so that the process then becomes a combination one belonging to Group IV.

In the manufacture of yellow soap resin is sometimes added to the partly finished soap, so that resin acids become neutralised by the alkali, and the resulting resinates intermix with the fatty acid soaps *pari passu* with their formation; it is, however, in most cases preferable to dissolve the resin in strong alkaline ley separately, and add the resulting mass of resinate to the fatty acid soap towards the last stage of its preparation. So far as this method of preparing resinate is concerned, the process is practically identical with the manufacture of soap proper by direct intermixture of red oils and strong soda ley as above described.

In the treatment of scouring suds from dye works and similar factories the grease is often recovered in the form of free fatty acids, the suds themselves, or the product of their treatment with lime, &c., being acidulated with sulphuric or hydrochloric acid so as to separate the fatty acids; these recovered greases are converted into coarse soap in exactly the same way as red oil.

In all these operations a very useful appliance is the 'steam twirl,' consisting of a hollow agitator made of a convoluted tube capable of revolving round a vertical axis, and connected by means of a hollow spindle with the steam supply. The tube being perforated at intervals with a series of small holes, continuous jets of steam pass into the mass from the agitator whilst in use, not only causing more perfect intermixture, but also heating up the whole mass by blowing steam through it.

Group II. The processes in which soap is prepared by saponification of glycerides, without subsequent separation of the glycerin set free, are conveniently sub-divisible into three classes, according as the materials are below a boiling heat (so called 'cold processes'), or are boiled in open pans under ordinary atmospheric pressure (as in the manufacture of soft soap and marine soap), or are treated at temperatures above the boiling-point in closed vessels under increased pressure, a method of working which has come into some considerable degree of use in certain districts, notwithstanding some practical difficulties in carrying it into successful operation.

Cold process soaps. In the manufacture of toilet soaps, as carried out by perfumers and others working on a comparatively small scale (whence the term 'little-pan soaps' sometimes applied to the products thus obtained), 'cold' processes have long been in use, on account of the simplicity of the appliances requisite, a pan and some agitating arrangement being the only essentials. The mixture of oils, fats, &c., intended to be saponified is rendered fluid by the application of a gentle heat, and is then thoroughly intermixed with the appropriate quantity of alkaline ley of suitable strength, also previously warmed to a temperature usually considerably short of boiling-point. The mass is then set by for some time, and well covered up so as to keep in the heat; usually the saponification does not proceed at any considerable rate until after the expiration of some little time, when the mass begins to increase perceptibly in temperature through the development of heat during the chemical change going on. When perfumed soap is thus made, the process is carried out at as low a temperature as possible, in order to avoid the injury to the scent apt to be caused by long exposure to higher degrees of heat; accordingly, it often happens in soaps of this class that the action is more or less incomplete, so that the soap ultimately obtained contains more or less considerable amounts of unsaponified fatty matters, and of uncombined alkali that have failed to react on one another. Of late years a variety of 'transparent' soaps has been largely sold prepared by a similar process, a large percentage of ordinary *sugar* being added to the mixture in the form of syrup, so that the total mass when finished often contains upwards of half its weight of sugar and water jointly. With suitably selected oleaginous mixtures (castor oil being an ingredient specially suitable, mixed with more or less lard or tallow, and cocoanut oil, &c.), and an excess of alkaline matter (which seems to be necessary to avoid muddiness and semi-opacity due to defective saponification), a perfectly clear mass is thus obtainable, which in practice is generally tinted yellow orange or red by incorporation of a small quantity of appropriate soluble colouring matter (usually a coal-tar dye-stuff). The products thus formed, though frequently pretty enough to look at, are often of the vilest quality imaginable, from the point of view of liability to injure the skin when used for ablution, owing to the large amount of alkali in a free state present, and the rapidity with which the mass dissolves in water when used. In some of the better class of soaps of this kind, the transparency is brought about by the use of more or less alcohol as an ingredient in the mass, whereby the amount of sugar otherwise necessary may be diminished; glycerin may be advantageously substituted for sugar, as the latter has a marked tendency to affect tender skins injuriously, but this is rarely done on account of the increased cost. The following formula and directions may be quoted as a sample of the method adopted in the preparation of cheap cold-process transparent soaps[1] (S. C. I. April 1883):—

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[1] Transparent soaps produced by the cold process must not be confounded with the older class of transparent soaps prepared by dissolving dried soap of good quality in alcohol, *v.* p. 418.

'Melt the following with agitation:—10 kilos. cocoanut oil, 10 kilos. castor oil, 8 kilos. neutral tallow, and saponify them at 50°C. with 14 kilos. of caustic soda at 38°Bé., and continue stirring until pastiness sets in. Add 8 kilos. loaf sugar in $8\frac{1}{2}$ litres of water at 85°C., taking care to bring it in gradually. As soon as the soap begins to solidify at the sides the boiler is jacketed with a water-bath kept at 80°C. until it has attained the proper consistency and the scum has separated. Add 20 to 30 per cent. of loading, agitate well, and then stir in a boiling solution of 1 kilo. crystallised soda in 1 litre of water; dye, perfume, and finish off the batch as usual.' The 'loading' referred to is prepared from petroleum deodorised by means of bleaching powder and hydrochloric acid, and treating with chalk to remove acid: '30 kilos of perfumed oil are heated to 50°C., mixed with 2 kilos. of well-dried soap shavings, and heated until a sample on being taken out solidifies on cooling.' These directions will give a product containing about 13 per cent. of sugar, and only about 35 per cent. of actual soap; whilst the total alkali used is about $\frac{9}{8}$ of the quantity equivalent to the fatty matter, so that a large amount of surplus alkali must necessarily be present, to the great injury of the skin of the user of the soap, if unfortunately sensitive to such agents.

A 'cold' process for converting tallow and other fats into soap on a comparatively large scale (2 to 3 tons of fatty matter at a time) was introduced by Hawes some years ago, but has not been very widely adopted, probably on account of the difficulty of ensuring complete saponification. In working this process the melted tallow is placed in a cylindrical vessel furnished with an agitator (preferably arranged horizontally), and the appropriate quantity of strong caustic ley run in at such a temperature as will keep the fatty matter fluid. The agitator is then worked for some three or four hours, after which the thickened mass is run off into another vessel, and allowed to stand some days, to allow of the completion of the action as far as practicable.

Soft soap. In the manufacture of potash soaps of this class drying vegetable oils are usually employed, such as linseed, poppy, and hempseed oils; olive and cottonseed oils and 'oleine' are sometimes used with more or less train or seal oil, or fish oils, such as cod oil. Some palm oil or tallow is generally also added, in order that the finished product may contain a small percentage of potassium palmitite or stearate, which separates out at temperatures near to 12°C. in a solid crystalline state, producing an appearance known as 'figging,' from its resemblance to the seeds of a fig, and supposed to indicate superior quality, although on what grounds it is somewhat difficult to understand. Vegetable oils, especially hempseed oil, usually communicate a greenish shade, often imitated in soaps made from other materials by addition of ultramarine or indigo. Bleached materials are preferred when a light-coloured product is required. The mixed oils to be saponified are heated in a copper, and potash ley run in in quantity insufficient to saponify the resin; the whole is then boiled together for some time, further additions of ley, and sometimes also of oils, being made from time to time until a sample taken out and allowed to cool appears a homogeneous jelly, free from admixed surplus ley or undecomposed oil. To attain this point accurately requires considerable experience and judgment on the part of the workman. Usually the first leys are much weaker than those subsequently employed when the action is well started, and often they contain an admixture of carbonated alkali with the caustic potash; the strength of the leys employed, and the time of boiling (and consequently the amount of evaporation taking place), require to be carefully proportioned to one another, so as to leave in the finished mass the required amount of water, which usually varies between 30 and 50 p.c. Soda is sometimes admixed with the potash used to the extent of 25 to 35 p.c. of the total alkali. If too large a proportion be used, the product is apt to exhibit muddiness and want of translucency, more especially in cold weather. Soaps made from linseed oil are said to resist this tendency best, so that during severe frost this oil alone and potash without soda are preferable in order to secure a product presenting the physical appearance regarded as indicative of good quality; whilst in warmer weather, and especially in summer, other oils and mixtures of oils, and potash containing soda may be employed with safety. Resin is frequently used as an ingredient in soft soap, the palest sorts only being employed when the colour of the product is unimportant; this admixture, however, and still more that of silicate, is highly objectionable in soaps intended for fulling woollen goods, on account of the injury thereby caused to the fibre. Any considerable excess of alkali (in practice impossible wholly to avoid if complete saponication is to be effected) is also deleterious for the same reason. For household and general scouring purposes, on the other hand, such admixtures are by no means so injurious, as they rather increase the detergent power than communicate any really hurtful quality. The addition of such weighting materials as glue, starch, clay, and the like is, of course, an entirely different kind of thing, such admixtures serving no good purpose whatever, and being adulterations pure and simple.

The pans or coppers used in the manufacture of soft soap are usually heated by direct firing. In order to prevent frothing over, a 'fan' is often employed, consisting of a set of vanes rotating on a horizontal axle, so arranged that the fan can be lowered into the pan to any required depth, and, by revolving just above the surface of the contents, break the foam and bubbles and so prevent frothing over.

Marine soaps are prepared in much the same way as soft soap, with the exception that soda is the alkali, and cocoanut or palmnut oil the main or even the sole ingredient in the mixture of fats and oils used. Cocoanut oil does not saponify as readily as many other fats, requiring a pretty strong ley to effect decomposition; but when the action once starts it goes on rapidly. Usually the resulting product is intermixed with silicate of soda, whereby increased detergence is gained. On account of the power possessed by cocoanut oil soda soaps of forming a firm mass, even when largely admixed with water, especially in contact with saline and alkaline salts, it often happens that scouring soaps of the marine class contain but little true soap, as much as 80 to 85 p.c. of the mass being water, silicate of soda, extra alkali and salts, and only 15–20 p.c. genuine soap.

Soaps prepared under increased pressure. In order to avoid the incomplete saponification liable to be effected when so-called 'cold' processes are used, various methods have been patented in which this fault is avoided by employing a higher temperature, produced by increased pressure. Amongst these may be specially noticed Dunn's process, in which the fats to be saponified (*e.g.* a mixture of tallow, palm oil, and resin) are placed in a boiler along with the equivalent amount of caustic soda ley, and the temperature then raised until a pressure of from 1 to 4 atmospheres is indicated, according to the degree of ease with which the materials saponify. After about an hour the action is complete, and the mass of finished soap is run out into frames to cool and solidify. In Bennett and Gibb's method, higher pressures (15 to 20 atmospheres) are employed, whilst carbonated alkali is used instead of caustic. An agitator keeps the mass well intermixed, and a continuous action is maintained, fresh materials being constantly pumped in at one end of the boiler whilst the finished soap emerges at the other end.

Group III. At the present day by far the largest proportion of scouring and fulling soaps, especially those of the laundry and household class, are still made by the old process of 'soap boiling' so carried out that the complementary product, glycerin, is not retained in the finished soap; the chief difference between the plant in a modern soapery and that in use some decades ago lying in the dimensions of the boiling pans (sometimes termed 'coppers' or 'kettles'), which have gradually increased in size from a capacity of only a few tons or even hundredweights up to 30 or 40 tons and upwards; and in the substitution of 'wet' or 'dry' steam for free fire as heating agent, the former being employed when dilution of the mass with condensed water is immaterial, and the latter when this has to be avoided or when evaporation is to be carried on. Frequently the pan is fitted with both sets of steam coils, so that 'wet' steam can be blown through the mass by turning on the steam direct from the boiler into the one coil whence the steam escapes through a series of perforations; or, when required, 'dry' (*i.e.* high-pressure or superheated) steam can be passed through the other coil, such steam not escaping into the copper itself, but simply circulating through the worm or heating coil.

Three classes of boiled soaps may be distinguished, respectively known as *curd*, *mottled*, and *fitted* soaps; the distinction between the three mainly lying in the manipulation adopted in the later stages of manufacture, whereby certain differences of texture and composition are brought about. In all cases the first stage consists of 'killing the goods'—*i.e.* converting by partial saponification the melted fats and oils into a kind of emulsion. For this purpose comparatively weak leys are usually employed, at first of about sp.gr. 1·05, as stronger ones do not act so readily upon fresh fatty matter. When, by boiling up such leys and the 'goods' the action is well started, somewhat stronger leys are gradually run in, and more goods, if the whole quota were not employed at first. Ultimately, when nearly but not quite, enough alkali has been added to bring about complete saponification, and the boiling has been properly carried out, a semi-fluid mass results, containing the partly-formed soap in what is termed a 'close' state—*i.e.* mechanically mixed to a homogeneous paste with a considerable excess of water containing glycerin in solution. The next step is termed 'graining,' and consists in the addition of salt either in the solid state or as strong brine, the effect of which is to render the soap insoluble, so that a curdy mass separates and floats up to the top, whilst an aqueous briny solution of glycerin falls to the bottom, after standing awhile. If the operation has been properly conducted, the latter will retain practically no soda in the caustic state, whilst the soap has been completely thrown out of solution, so that no oily matter separates on addition of an acid to the aqueous liquid. The 'spent leys' are then run off, and the saponification completed by further boiling the separated curd with a succession of fresh caustic leys until a distinct alkaline taste remains persistent after long boiling. If mottled soap of genuine character is to be made, and the curd is boiled with leys of the right strength, the mass resulting at this stage simply requires running into the cooling frames, after separation of the leys by subsidence, and, in some cases, addition of colouring pigments. When the mass possesses the proper physical texture (a point known only by observation and experience) the peculiar result is brought about that all colouring matter, whether derived from impurities in the original soap or subsequently added, segregates in veins as the mass solidifies during cooling, so that when cold the block exhibits a 'mottled' appearance when cut across. With Castile and Marseilles olive oil soaps of old-fashioned type this segregation does not take place if the proportion of water present exceeds a certain limiting amount (about 20 p.c.), the soap being then so fluid that the colouring matters entirely subside to the bottom before cooling is effected; wherefore the existence of a mottled structure has come to be regarded as evidence of good quality—*i.e.* freedom from too large a proportion of water. Of late years, however, it has been found that the same phenomena of mottling can be brought about in soap heavily watered, by adopting certain methods of manipulation—*e.g.* addition of a certain proportion of silicate, which thickens the texture, and stirring, while cooling, until the mass becomes stiff enough to prevent separation of colouring matter otherwise than in veins; so that mottled soap of modern make and that of the older type are by no means the same thing as regards composition and quality.

When a white curd soap is to be made, the completely saponified soap paste is put through a finishing operation consisting of a kind of washing or dilution with water or weak leys, and allowing to stand, whereby coloured impurities subside; the cleansed curd is then boiled down until the flakes present a particular appearance dependent on the amount of water retained, which again depends on the strength to which the ley has been boiled. After standing to allow the leys to separate, the acid is run into the cooling frames, and concretes on cooling to a white mass usually containing more or less alkaline ley mechanically entangled, and consequently somewhat alkaline in character as a whole.

The operation of 'fitting' is in principle much the same; the soap paste is allowed to stand some hours and the leys run off, and the whole then heated up with wet steam—and, if need be, weak leys—until a peculiar texture termed the 'fit' is attained, when the whole mass is allowed to remain at rest some days, according to the size of the pan. During this time the contents separate into three layers—uppermost, a frothy soap, known as the 'fob'; at bottom, aqueous liquors and dirty impurities that have subsided, termed the 'niger'; and in the middle, the cleansed or 'neat' soap, ready to run into the frames. Resin soaps are those most usually fitted, and ordinarily contain (when fresh and undried by storage, and if not intentionally weakened by dilution) some 30 p.c. of water. Inasmuch as boiling down is not requisite in the case of fitted soaps, as it is with curd and genuine mottled soaps, a close steam worm is not indispensable for the fitting pan, wet steam sufficing to carry out the entire operation if so desired. Owing to the mode of preparation a well-fitted soap is necessarily almost wholly free from any excess of alkaline matter, whereas curd and mottled soaps often contain considerable quantities of alkaline matter derived from the leys, or even intentionally added by intermixture in the soap frame as 'hardening' agents—*i.e.* materials tending to give a fictitious stiffness and consistency to the mass, and so to disguise 'letting down' by copious watering. The art of thus 'making water stand upright' is now so widely practised through competition as to be regarded by manufacturers as one of the normal operations of the soap factory.

Group IV. Soaps prepared by combinations of the various processes of the preceding three groups are of comparatively small importance, the chief being those where mixtures of unsaponified fatty matters and red oils or other free fatty acids are worked together, being usually boiled up and treated precisely as in the case of unsaponified fats alone when treated by methods belonging to the third group. Resin soaps also are sometimes made by adding resin gradually to nearly finished soap, prepared by boiling after separation of the earlier spent leys and during the subsequent boiling with fresh leys. In this case resinate of soda is gradually formed and intermixed with the soap proper; and in the same way potash resinate is sometimes formed and incorporated with true soft soap, by gradually adding resin during the later stages of soft soap boiling. Preferably, however, the resin is separately dissolved in alkaline ley, and the fluid thus obtained directly intermixed with the boiled soap in the latest stage of the operations just before fitting and finishing.

Group V. *Processes employed subsequently to saponification.* By whichever of the foregoing methods soap may have been formed originally, it is ultimately obtained as a more or less soft, warm, or hot mass, which is run into 'frames' to cool and solidify. These frames are made of iron plates or of wooden bars, in such a way as to be readily taken to pieces and put together again as required, the separate portions being held together by rods terminating in screws and furnished with nuts, the size varying with circumstances from a capacity of 1 cwt. or less for choice kinds of toilet soaps up to a ton and upwards for household soaps. When quite cold the frame is dismantled so as to leave a block of soap the size of the interior of the frame. This is cut into slabs by means of a cutting wire pulled horizontally through the mass by hand or machine, and these are similarly cut transversely into bars, usually of about 3 lbs. in weight. The bars thus produced are generally piled loosely on one another so as to dry them slightly externally and case-harden them; occasionally the same result is obtained with less loss of weight by immersion in brine. In certain cases various ingredients are well 'crutched' or stirred into the mass whilst still semi-solid before cooling—*e.g.* water, silicate of soda, solution of sulphate of soda, or soda ash, or other aqueous fluids—as diluting or hardening agents; nitrobenzene to disguise tallowy or rancid odour, and communicate almond-like perfume; carbolic acid and other analogous substances in the preparation of sanitary and disinfectant soaps; and so on. With highly-watered soaps, or where for any reason there is a liability to separation between the soap and ingredients added, the crutching is kept up in the frame until the mass has cooled down and stiffened so thoroughly as to prevent any future segregation taking place. When the substances incorporated are volatile, on the other hand, as little stirring as possible is used consistent with due intermixture, and the frame is covered to diminish volatilisation.

When the soap dealt with is of superior quality, intended for toilet purposes, various subsidiary operations are often gone through for the purpose of improving its nature. Of these, *remelting* in a steam-jacketed pan is one frequently practised, the object here being generally to blend together several kinds of soaps, or to improve the texture of the product. After incorporation with the mass of the appropriate perfumes and other ingredients —such as bees-wax, spermaceti, glycerin, &c.— the whole is recast in smaller frames and then cut up into slabs and bars, and finally into smaller masses, which are then stamped into tablets in machines provided with dies very much after the fashion of rough coining and medal presses, excepting as regards the way in which the pressure is communicated, foot or hand power being often employed. In order to improve the texture of certain soda soap blends, a quantity of pearlash dissolved in water is sometimes added to the fused mass before running into the frames. The effect of this, as already noticed, is to produce a quantity of potash soap and sodium carbonate equivalent to the potassium carbonate thus added; so that the finished soap has the disadvantage of containing still more free alkali than the original materials. A process introduced by the author has for its object the opposite result of diminishing the free alkali present.

This is effected by adding to the mass a weighed quantity of sal-ammoniac (or other suitable ammoniacal salt) proportionate to the alkalinity to be destroyed; the ammoniacal compound is thus resolved into free ammonia, which escapes (either at once or subsequently), whilst the acid constituent of the salt neutralises the alkali required to be destroyed.

The process of *milling* is one used for certain of the more expensive kinds of toilet soaps, and inasmuch as heat is avoided thereby, it is peculiarly applicable to the more delicately perfumed varieties. The stock soaps employed as basis, preferably of the finest quality obtainable, are reduced to shavings by a machine acting on the principle of a rotary plane; these are then partly dried so as to diminish the amount of water present, and are then ground between rollers along with the colouring matters, perfumes, and other ingredients required. Ultimately, a stiff putty-like mass is obtained, which is forced by screw or hydraulic pressure through an orifice so as to shape it into bars, which are then cut into short lengths and the pieces stamped into tablets.[1]

One of the most elegant forms of toilet soap is one which unfortunately is much less frequently met with in the trade than cheaper and far inferior productions; this is soap rendered transparent by drying to render anhydrous, solution in alcohol, and distilling off the solvent. Most soaps thus treated yield residues possessing more or less transparency after tolerably complete expulsion of remaining alcohol by long exposure to air, those prepared with the finer kinds of resin being especially suitable, particularly if an addition of glycerin to the mass be made before the spirit is volatilised. For the sake of cheapness, however, most of the spirit-process transparent soap sold is made by substituting methylated spirit for pure alcohol, and sugar for glycerin; the effect of which, especially when relatively coarse fatty matters are used as basis of the stock soap, is vastly to deteriorate the quality of the product. This is generally devoid of 'free alkali,' that being left undissolved (as carbonate) by the spirit; but the advantage thus gained is more than lost by the presence of sugar, that substance having a most objectionable effect on tender and sensitive skins.

Analysis and valuation of soap. According to the special purpose for which any given kind of soap is required, so are various requirements more particularly important than others. Thus, if a soap is intended for scouring woollen goods or for application to the skin, the most important characters are freedom from excess of alkaline matter that might otherwise act injuriously, and suitability in physical properties (as regards solubility &c.), and in the chemical nature of the fatty matters used; whereas, for many household purposes—*e.g.* scrubbing floors, &c.—the presence of an extra amount of alkali besides that present combined with fatty acids is likely to be beneficial rather than the reverse. In all cases an important consideration is the amount of water present and that of foreign matters added, either as weight-giving 'filling,' or to increase the firmness of the mass and give it a fictitious appearance of solidity. Amongst substances of this latter class salts of an alkaline reaction, especially alkaline carbonates, when added to scouring soaps are least objectionable, inasmuch as they more or less increase the detergent power; whilst neutral salts, such as sulphate of soda, and inert solid matter, such as farina, pipeclay, or chalk, are of absolutely no value, excepting in so far as they more or less prevent wasting during use through softening and dissolving too quickly. An imperfectly made soap containing much unsaponified fatty matter, or one containing an undue admixture of water, petroleum, sugar, or other diluting agents, is obviously valueless to the consumer so far as the ingredients other than soap are concerned. Accordingly, the most useful determinations in forming an opinion as to the character and value of a given soap are those which will lead to the knowledge of the amount of actual soap present, the nature of the fatty materials used in its preparation, the quantity of surplus alkali present in forms other than soap (*i.e.* other than resinates and alkali salts of fatty acids), and the nature and amount of the other ingredients besides water (if any). Moreover, in medicated soaps the presence of a due amount of the active constituent incorporated is a most important point, as similarly in sanitary and disinfecting soaps—*e.g.* the amount of phenol in a 'carbolic acid soap'—wherefore the determination of such substances in soaps of this class is usually that most required.

In general, a fair notion of the character of a soap may be obtained by determining the following quantities:

1. Amount of fatty and resinous acids produced on decomposition by a mineral acid. If unsaponified fat and certain other substances (paraffin, uncombined resin, &c.), insoluble in water but liable to be mixed with the liberated fatty acids, be present, their amount (and nature) must be determined in order to correct the first value as directly obtained. Commercial soaps almost invariably contain a small quantity of such matters, usually less than one per cent. if the soap have been made from natural fatty and oily materials, but considerably exceeding this amount in other cases where additions of such substances have been purposely made.

2. The total alkalinity of the soap expressed as anhydrous oxide of sodium (or potassium).

3. The alkalinity due to substances other than soap similarly expressed.

The percentage of actual soap present is then known by adding together the amount of alkali present as soap (the difference between the values 2 and 3) and that of fatty acids (value 1 after correction, if need be, as above), and subtracting from the sum the amount of water taken up during decomposition of the soap and liberation of the fatty acid. This amount is obviously $\frac{9}{31}$ of the combined alkali expressed as anhydrous sodium oxide Na_2O; or $\frac{9}{47}$ of that expressed as anhydrous potassium oxide, K_2O; for, supposing sodium stearate is dealt with, the reaction of decomposition into fatty acid and anhydrous sodium oxide may be written $2Na.C_{18}H_{35}O_2 + H_2O = 2C_{18}H_{36}O_2 + Na_2O$; and similarly in other cases. Expressed in symbols, if a = fatty acids (corrected as above), b = total alkali, and c = alkali other than soap in 100 parts of soap, then the percentage of actual soap is $a + b - c - \frac{9}{31}(b-c) = a + \frac{22}{31}(b-c)$ if the alkali be soda; and $a + b - c - \frac{9}{47}(b-c) = a + \frac{38}{47}(b-c)$ if it be potash.

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[1] An analogous process has been patented by the author whereby hot fluid soap is passed through cooling tubes, and whilst still pasty pressed through an adjutage so as to emerge in the form of a solid bar, whereby the operations of casting in frames and cutting up are dispensed with.

In stating the results of an analysis, it is usual to make the total determinations sum up to 100. If, however, all the constituents of a soap be determined, the fatty acids being weighed as above, the sum will obviously exceed 100 by a quantity equal to the weight of water taken up during decomposition—viz. $\frac{9}{31}(b-c)$ in the case of soda-soap, and $\frac{9}{47}(b-c)$ with a potash soap. To obviate this it is usual to calculate the value of $a - \frac{9}{31}(b-c)$ or of $a - \frac{9}{47}(b-c)$, *i.e.* the corrected fatty acids, less the water taken up during decomposition of the soap by acid, and to state it as 'fatty anhydrides.' Thus, if on analysis a soda-soap gave the figures: Fatty acids 65·25 p.c., total alkali 8·55, combined alkali 0·85: the value of $a - \frac{9}{31}(b-c)$ would be $65\cdot25 - \frac{9}{31} \times 7\cdot70 = 63\cdot03$, and the analysis would be stated thus:—

$$\begin{array}{ll} \left.\begin{array}{l}\text{Fatty anhydrides}\\ \text{Combined alkali}\end{array}\right. & \left.\begin{array}{r}63\cdot03\\ 7\cdot70\end{array}\right\} = 70\cdot73 \text{ p.c. of actual soap} \\ \left.\begin{array}{l}\text{Water, free alkali,}\\ \text{saline matters, \&c.}\end{array}\right\} & 29\cdot27 \left\{\begin{array}{l}\text{containing}\ \cdot85 \text{ p.c.}\\ \text{free alkali}\end{array}\right. \\ \hline & 100\cdot00 \end{array}$$

the alkali throughout being expressed as Na_2O.

The amount of actual soap present being thus known, additional valuations of the other constituents present (water, sodium chloride, and other neutral salts, silicate, sugar, &c., &c.), can be proceeded with if required; but in most cases an examination of the fatty acids set free with a view to determining approximately their nature will suffice. For this purpose the melting-point, general physical properties, odour, and especially their mean molecular weight frequently render service. The last is readily calculable from the amount of fatty acid and combined alkali found as above; since if x be the mean molecular weight required, $31 : x :: b-c : a$ if the alkali be soda, and $47 : x :: b-c : a$ if potash; whence $x = 31 \times \frac{a}{b-c}$ for soda soap, and $x = 47 \times \frac{a}{b-c}$ for potash soap.

For example, a soap yielding fatty acids = 60 p.c., and combined soda = 8·0 p.c., would give the value for $x = 31 \times \frac{60}{8} = 232\cdot5$; a figure which would at once suggest that a considerable amount of cocoanut or palm-nut oil had been used amongst the fatty matters from which the soap was made, inasmuch as these oils give fatty acids of mean molecular weight of 200 or less, whilst the molecular weight of palmitic acid (the lowest of the other fatty acids usually met with) is 256.

The following table exhibits the values of x for the leading pure fatty acids, and various mixtures obtained from ordinary sources—*i.e.* common fats and oils—according to the author's experience; very similar values are deducible from the results published by other observers:—

Acid	Formula	Molecular Weight
Brassic . .	$C_{22}H_{42}O_2$	338
Arachidic . .	$C_{20}H_{40}O_2$	312
Ricinoleic . .	$C_{18}H_{34}O_3$	298
Stearic . .	$C_{18}H_{36}O_2$	284
Oleic . . .	$C_{18}H_{34}O_2$	282
Linoleic . .	$C_{18}H_{32}O_2$	280
Palmitic . .	$C_{16}H_{32}O_2$	256
Physetoleic .	$C_{16}H_{30}O_2$	254
Myristic . .	$C_{14}H_{28}O_2$	228
Lauric . .	$C_{12}H_{24}O_2$	200
Fatty acids from tallow, lard, and cotton-seed oil . .	Chiefly $C_{18}H_{36}O_2$ and $C_{18}H_{34}O_2$ with a little $C_{16}H_{32}O_2$	270 to 285
Ditto from castor oil . . .	Mostly $C_{18}H_{34}O_3$	290 to 295
Ditto from cocoa-nut oil . .	Lauric acid $C_{12}H_{24}O_2$ with lower and higher homologues	195 to 200
Ditto from mixtures of tallow and palm oil .	$C_{18}H_{36}O_2$, $C_{18}H_{34}O_2$, and $C_{16}H_{32}O_2$	260 to 270

Analytical process.—I. *Fatty acids produced on decomposition by a mineral acid.* A weighed quantity of soap is dissolved in hot water, and sufficient mineral acid added to produce complete decomposition after thorough stirring. On standing, the liberated fatty and resinous acids float up to the top, and solidify to a more or less soft cake, which may be carefully removed, dried, and weighed. For this mode of procedure at least five, and preferably ten or twenty, grms. of soap should be taken. If the cake is too soft to bear handling, a weighed quantity of high melting paraffin wax, bees-wax, or some similar material should be added to the hot mass after stirring with the mineral acid, and the weight deducted from that of the dried cake ultimately obtained. Instead of allowing a cake to separate by cooling, the hot fluid may be transferred to a separator provided with a stopcock, and when sufficiently cool shaken up with ether or the lightest petroleum spirit. This dissolves the fatty acid, so that two layers of liquid are obtained, the lower one an aqueous liquor which is run off, and the upper one the ethereal or spirit solution of fatty acids, which is collected and evaporated to dryness and the fatty acids left weighed. Operating in this way, one to two grms. of soap will generally be found a more convenient quantity to deal with than larger amounts.

To obtain a correction for unsaponified fat, &c., a weighed quantity of soap is thoroughly dried, powdered, and treated with ether or lightest petroleum spirit as long as anything is dissolved out. The extract thus obtained yields on evaporation to dryness the uncombined resin, unsaponified fatty matter, non-volatile hydrocarbons, and similar substances that may have been present in the soap, and that were necessarily weighed along with the true fatty acids in the previous determination. Another method of manipulation is to dissolve the soap in a minimum of hot water, transfer to a separator, and agitate repeatedly with petroleum spirit or ether as soon as the temperature is sufficiently lowered to permit of this being done safely. The residue left on evaporation of the extract thus obtained generally contains traces of soap when ether is employed as solvent, wherefore petroleum spirit is preferable, provided it is sufficiently volatile to cause no increment in weight when a known quantity of bees-wax or paraffin is dissolved therein, and the solution again evaporated to dryness.

II. *Total alkali present.* This determination can generally be conveniently combined with that of fatty acids by using a known volume of standardised sulphuric, nitric, or hydrochloric acid to decompose the soap. After separation of fatty acids (as a cake or by a solvent) the aqueous liquid is titrated back by a standardised alkaline solution, so that the volume of acid neutralised by the alkali in the soap is known. If pure nitric acid be used and an alkaline solution free from sulphates and chlorides, the neutralised fluid resulting after back-titration can be divided into two portions, used respectively for the determination of the sulphates and chlorides present in the soap, should it be required to determine their amount. Of the various acid and alkali colour indicators available during titration, cochineal tincture is usually one of the most convenient, as any undecomposed soap ordinarily reacts alkaline therewith, whilst the colour change is more readily visible by gaslight than that of many other indicators.

III. *Free alkali.* A weighed quantity of soap, preferably freed from unsaponified fat by means of petroleum spirit as above described, is dissolved in hot alcohol as nearly anhydrous as possible. Ordinary methylated spirit usually suffices if the soap is not a very moist one. The hot fluid is filtered through a hot water filter, and a little phenol phthalein added to the filtrate. If a red colour is visible the amount of alkalinity is determined by dropping in a standardised acid solution (preferably alcoholic). If no colour is visible, a similar alkaline solution is used to determine any acidity (*negative alkalinity*). The filter, after well washing with alcohol, is treated with water and the alkalinity of the solution determined. The algebraic sum of this and the other positive or negative alkalinity of the filtrate represents the 'free alkali.' Most soaps thus treated yield a practically neutral filtrate, and a residue of sodium carbonate (or silicate, &c.) on the filter. If the filtrate is strongly alkaline, the soap contains *caustic* soda or potash to the extent thus indicated; this, however, seldom occurs in practice, excepting with very freshly made soaps, as the caustic alkali originally present becomes rapidly carbonated by exposure of the soap to the air. In such a case, any unsaponified fat present must be removed before solution in alcohol, otherwise the caustic alkali present will become partly neutralised by the fatty acids contained in the fat in virtue of the saponification brought about. Acidity in the filtrate may be sometimes brought about to a minute extent by the action of carbonic acid during filtration, whereby a trace of di-acid salt (stearate, oleate, &c.), soluble in alcohol, is formed, together with a corresponding amount of alkaline carbonate insoluble therein.

IV. *Examination for other constituents.* Substances insoluble in alcohol—such as *starch*, *bran*, *fine sand*, *china clay*, *pigments*, and similar matters—are for the most part left on the filter used in the previous determination if alkaline carbonates, &c., are dissolved thereoff by water. The SiO_2 present as silicate is best determined by incinerating a known weight of soap, evaporating the ashes to dryness with hydrochloric acid, and separating silica in the usual way. *Chlorides* and *sulphates* may be determined as above when nitric acid is used to separate fatty acids, or in separate portions from which the fatty acids are separated before precipitating with silver nitrate or barium nitrate. *Glycerin* and *sugar*, when present simultaneously, are not very easy to determine accurately. *Cane sugar* may be inverted and determined by Fehling's solution, using for the purpose a portion of the liquid from which the fatty acids have separated after acidification; and the glycerin may be at least approximately found by conversion into oxalate by means of permanganate. When present alone the *glycerin* may also be found by separating fatty acids by excess of sulphuric acid, exactly neutralising with sodium carbonate, evaporating to dryness, and treating the residue with alcohol, the extract being purified by evaporation and solution in absolute alcohol, and any mineral matter contained being estimated (by incineration) and subtracted.

When potash and soda are simultaneously present, the soap may be decomposed with hydrochloric acid, and the filtrate from separated fatty acids evaporated and treated with platinum chloride in the usual way.

Resin. It is sometimes desirable to determine the proportion between fatty acids proper and resin in resin soaps. Unfortunately no very accurate process appears to be available for this purpose. The one which in the author's hands has given the least unsatisfactory results is that due to Gladding (C. N., April 14, 1882), which consists in separating the fatty acid *plus* resin, dissolving about ·5 grm. in 95 per cent. alcohol, slightly supersaturating with alcoholic potash, and boiling to complete saponification (if imperfect),[1] making up to 100 c.c. after cooling with ether, and well agitating with finely-powdered silver nitrate. The effect of this is to form the silver salts of the resin acid present, which are soluble in ether, whilst the silver salts of ordinary fatty acids are insoluble therein, or nearly so; so that by filtering off a known fraction of the ethereal liquid, and shaking with dilute hydrochloric acid, there is ultimately obtained an ethereal solution of the free resin acids

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[1] Any unsaponified fat would be retained in ethereal solution subsequently, and ultimately weighed as resin.

Analyses of various typical kinds of soda soap.

—	'Primrose,' London make	'Ivory,' Canadian	'Cold water,' English	'Cold water,' Canadian	Oleic acid soap, London make	Imitation Castile soap, English
Fatty anhydrides	46·88	43·33	43·70	45·85	62·71	61·45
Resinous „	15·40	25·00	22·00	24·00	—	—
Combined alkali (Na_2O)	7·12	7·72	9·28	8·00	7·36	8·46
Sodium carbonate	·14	2·64	·58	2·22	·68	3·18
„ chloride	·14					1·17
„ sulphate	·07	21·31	24·44	19·93	29·25	1·23
Water with minute quantities of insoluble matters, lime, ferric oxide, &c.	30·25					24·51[1]
	100·00	100·00	100·00	100·00	100·00	100·00
Percentage of true soap	69·40	76·05	74·98	72·07	70·07	69·91
Free alkali (Na_2O)	·08	1·54	·34	1·30	·40	1·16
Mean molecular weight of fatty acids, &c.	280	283	230	280	273	234

[1] Including ·74 per cent. of insoluble pigments.

—	Mottled soap, old-fashioned (Lant Carpenter)	Mottled soap, modern (Lant Carpenter)	Best tallow curd, London make	Bleached palm oil, London make	Marine soap, non-silicated	Marine soap, silicated
Fatty anhydrides	62·5	46·6	66·60	66·20	32·00	13·50
Combined alkali (Na_2O)	7·0	5·2	7·51	7·83	5·20	2·27
Free alkali (including that present as silicate)	·6	·8	·50	·40	2·25	8·36
Silica (SiO_2)	—	1·3	—	—	—	10·50
Sodium chloride	·1	·8	1·35	2·05	7·65	5·05
Sodium sulphate	—	·3	·20	traces	1·45	·35
Water and insoluble matters, pigments, &c.	29·8	45·0	23·84	23·52	51·45	59·97
	100·0	100·0	100·00	100·00	100·00	100·00
Percentage of true soap	69·5	51·8	74·11	74·03	37·20	15·77
Mean molecular weight of fatty acids	285	287	284	271	290	197

Toilet Soaps.

—	High-class milled soap of Continental make	High-class opaque soap, English	Inferior opaque soap, English	Transparent soaps		
				Made by cold process	Made by spirit process	
					Sugared	Genuine, not sugared
Fatty anhydrides	83·60	60·20	65·00	38·90	65·60	68·10
Uncombined resin and unsaponified fats	1·00	—	—	·40	3·00	3·20
Combined alkali	9·80	6·98	8·91	5·57	7·73	7·62
Sodium carbonate	·24	·17	1·73	3·80	Nil	·20
Sugar	—	—	—	28·00	14·00	Nil
Glycerin	—	3·00	6·00	3·00	—	7·00
Water and minute quantities of salts	5·36	29·65	18·36	20·33	9·67	13·88
	100·00	100·00	100·00	100·00	100·00	100·00
Percentage of true soap	93·40	67·18	73·91	44·47	73·33	75·72
Free alkali (Na_2O)	·14	·10	1·01	2·22	Nil	·14
Mean molecular weight of fatty acids	274	276	226	225	272	286

themselves, which is evaporated and weighed. The main source of error is the uncertainty about the correction to be applied to allow for the solubility of the silver salts of the fatty acids present. Gladding considers that 100 c.c. of alcoholic ether dissolve ·0235 grm. (representing 4·7 per cent. of the mixture used when ·5 grm. is employed). The author's experience is that whilst this figure is not far from the truth with some kinds of fatty acids and mixtures thereof (*e.g.* oleic acid and cotton seed oil mixed, or stearic acid mixed with cocoanut oil), it is considerably different in other cases, stearic acid alone giving only about half the amount, and castor oil more than double the quantity (*v.* Alder Wright and Thompson, C. J. Abstracts of Proceedings, No. 20, 1886).[1]

Water. Usually the direct determination of water present is unnecessary, excepting as a check on the other values. A weighed quantity of the soap cut into thin shavings is heated in the water bath, and finally to 110°–115° in a hot-air bath until constant in weight, and the loss reckoned as water. Frequently the heating can be conveniently done in a weighed porcelain dish over a sand bath, the mass being carefully stirred with a glass rod (weighed along with the dish) until all moisture is expelled, usually indicated by the cessation of dew-deposition on a cold piece of glass placed for a few seconds over the dish.

The analyses on preceding page, made by the author when not otherwise stated, illustrate the composition of various typical kinds of soda soap. C. R. A. W.

SOAP-BARK. A few years since a peculiar bark was introduced into the European trade, and recommended to be employed instead of soap for washing and cleaning printed goods, woollens, and silks, especially for the delicate colours of ladies' dresses, &c. This soap-bark is externally black, but internally the liber consists of layers of yellowish-white. The bark is remarkable for its density, as it sinks in water. The cause of this is the great quantity of mineral substance in its ashes, there being 13·935 p.c. in the internal parts dried at low temperature, and 18·50 p.c. when dried at 100°C. The ashes consist largely of carbonate of lime, which forms 2·60 p.c. of the 13·935, and appears as small crystalline needles, isolated or in groups, in the cells of the liber, not only between its concentric rings but in every part of it. They glitter in the sun, resembling under the microscope the aragonite form of the crystallised carbonate of lime.

The soap-wort (*Saponaria officinalis*) is sometimes used for scouring and cleaning dresses. Several of this family of caryophyllaceous plants (*Dianthus*, *Lychnis*, *Gypsophila*, *Silene*) are remarkable for this property in a greater or less degree. By chemical means there has been extracted from these roots the *saponin* (or *struthiine*), a special substance, and to this, notwithstanding the very small quantity contained in the roots, the singular power is attributed of making emulsions, and of being used for soap in washing. The soap-wort of the Levant (*Gypsophila*) is, to this day, employed in the East for washing and cleaning silks and shawls. It is generally used in the Mediterranean districts of France and Spain; the French called it *herbe aux foulons* (the fuller's plant). The *Saponaire*, or *Savonière* of the French, is the root of a kind of Lychnis. Saponin was found by Henry and Boutron Charland in the bark of the *Quillaja Saponaria*, a tree of the family of rosaceous plants, and a native of Huanuco, in Peru. Ferdinand Lebauf made mention of this bark in 1850 for its richness in saponin, and recommended it for pharmaceutical use in preparing emulsions of oils, resins, balsams, and several other medicaments. He mentions likewise the bark of the *Yallhoy* (*Monnina polystachya*) as containing saponin. The fruits of *Sapindus Saponaria*, known as 'soap-berries,' are used in America and the West Indies for washing linen (Ure, 3, 853).

SOAPSTONE *v.* STEATITE.

SOAP-WORT. *Saponaria officinalis v.* SOAP-BARK.

SODIUM. Na. At. wt. 22·995.

Occurrence.—Sodium occurs as chloride in *rock salt* or *halite*, and in sea and other natural water. As nitrate it occurs in *soda nitre*, *nitratine*, or *Chili saltpetre*, forming large superficial deposits in Chili, Peru, &c. As sulphate, it is found in *Glauber's salts* or *mirabilite* $Na_2SO_410H_2O$; as carbonate in *natron*

$$Na_2CO_310H_2O,$$

and *trona* $Na_4C_3O_8.4H_2O$; and as double fluoride with aluminium, in *cryolite* $3NaF.AlF_3$. Among the rock-forming silicates it occurs in *oligoclase* (soda felspar) $2Al_2O_33SiO_2.2(Na_2O.CaO)3SiO_2$;

albite $Al_2O_33SiO_2Na_2O.3SiO_2$;

labradorite $Al_2O_32SiO_2Na_2O.SiO_2$;

sodalite $3(Al_2O_3SiO_2.Na_2O.SiO_2)2NaCl$;

analcime $Al_2O_3.3SiO_2.Na_2O.SiO_2.2H_2O$,

and many other silicates.

Preparation.—A *résumé* of the history and earlier methods of preparation of potassium and sodium has been given in the article on POTASSIUM.

The first method adopted for the preparation of sodium on the large scale was that of Deville, who substituted that metal for potassium in the manufacture of aluminium (Deville, 'De l'Aluminium,' Paris, 1859, 60, 120; A. Ch. 1856, 46, 415; D. P. J. 134, 369; 141, 303).

A mixture of 30 parts calcined sodium carbonate, 13 of coal, and 5 of chalk is calcined to render it more compact, and is then introduced into a mercury bottle *b* (fig. 1), which is placed in a furnace as shown. When the bottle attains a reddish-white heat, vapours of sodium appear at the mouth of the tube *d*, and burn with a bright flame. The condenser *e* is then applied to the tube, which only projects slightly beyond the furnace, in order to prevent obstruction by condensed metal. The condenser is of the form introduced by Mareska and Donny (A. Ch. [3] 35, 147; Mitscherlich, Lehrb. der Chem. 2, 10), and consists of a flat iron plate, fitting into the turned-up edges of a similar plate, thus forming a flat box with a large condensing surface. The turned-up edge at the outer end is dispensed with or cut away at the top, so that the metal runs out into a receiver containing naphtha, or remains in the condenser until filled. The plates are shaped to form a neck for receiving the tube *d*.

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[1] Since the above was written, a method has been introduced by Twitchell which gives satisfactory results; this consists in dissolving a weighed quantity of mixed, fatty, and resinous acids in absolute alcohol, and passing in dry hydrochloric acid gas. Fatty acids are thus converted into compound ethers, whilst resinous acids are unaffected; by adding water and ether an aqueous solution of hydrochloric acid is washed out on agitation, whilst an ethereal solution of neutral compound ethers and free resinous acids is obtained; by titrating this with standard alcoholic alkali, using phenol phthalein as indicator, the latter are readily determined (*v.* Analyst, 1891 [16] 169).

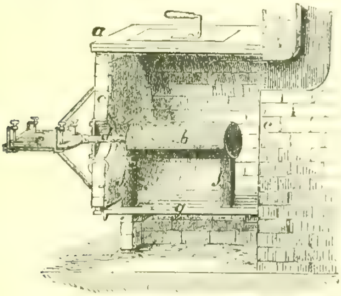

Fig. 1.

The temperature actually required for the reaction is about that used for the reduction of zinc, but a much higher heat is required to obtain the maximum result.

Fig. 2 shows an arrangement employed by Deville for the continuous preparation of sodium in wrought-iron cylinders, in a reverberatory furnace containing several of them. Each cylinder is closed at one end by a wrought-iron cap, *o*, and is fitted at the other end with a tube L, for connection with the condenser. The calcined mixture is introduced into the cylinders in canvas or paper bags, and the cap *o* is luted on with fireclay. When the distillation is finished the cap is removed, and the residue is replaced by a fresh charge. The cylinders are charged alternately. The explosive compound with carbon monoxide is not so troublesome, nor is it produced in such quantity as in the manufacture of potassium, being, in fact, usually not formed at all. A considerable quantity of impure sodium, however, adheres to the condensers, so that they require cleaning after each operation, the scrapings being stored and re-distilled.

More recently the chalk has been replaced by lime, 7 parts of which replace 5 of chalk. The temperature used for the reduction is about 1400°, and the production is under 40 p.c. of the theoretical yield in the case of sodium, or much less in the case of potassium. Small wrought-iron tubular retorts are employed. The injury to the plant is said to be double the price of the metal in the case of sodium. The *Scientific American* (1867, 100) describes the method formerly employed for making sodium by the Manchester Magnesium Metal Company.

It was not, however, until 1886 that any material alteration in Deville's process was introduced. In that year Castner invented a process in which sodium or potassium hydroxide is reduced by a so-called carbide of iron, having approximately the composition CFe_2, and prepared by adding finely-divided iron (obtained by passing producer gas over heated ferric oxide) to melted pitch, and coking the mixture in large cylinders.

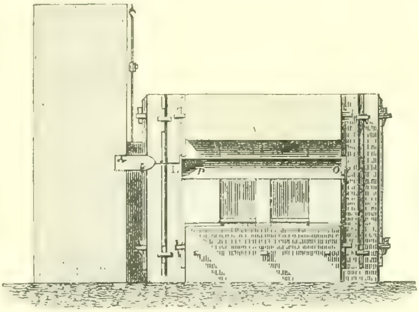

Fig. 2.

In the process formerly followed at the Aluminium Company's works at Oldbury, rather more of the finely-powdered 'carbide' is mixed with caustic soda than is required by the equation $6NaHO + C_2 = 2Na_2CO_3 + 3H_2 + Na_2$. A certain proportion of carbon monoxide is also produced by a secondary action of the excess of carbon on the sodium carbonate (Mactear, S. C. I. 1887, 174).

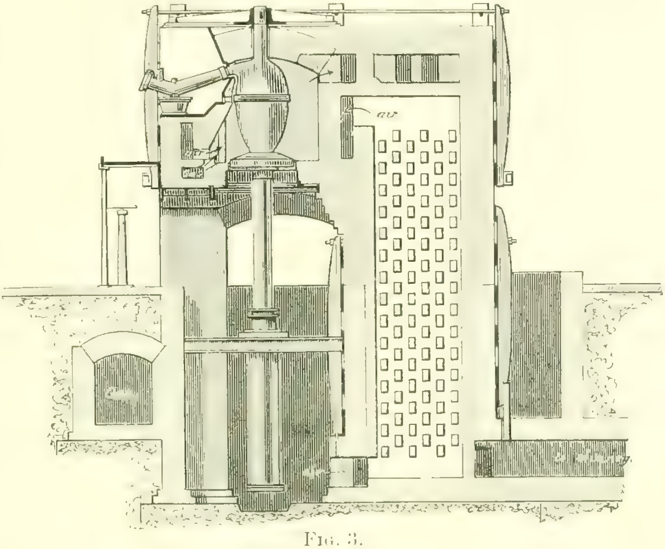

Fig. 3.

Each furnace contains five egg-shaped retorts, three feet high, and half that width at the broadest part, heated by regenerative gas burners (*v.* fig. 3). The cover of each retort has a vertical pipe passing through the top of the furnace, and serving for introduction of part of the charge, and a lateral branch leading to a cast-iron condenser of peculiar form, about 5 inches in diameter, and nearly 3 feet long, with a small opening in its inclined bottom about 20 inches from the nozzle. A small hinged door to the condenser permits examination by the workman, and a hinged rod provides for removal of any obstruction in the conducting tube. The condensed metal runs out into a pot placed beneath the opening, and, when sufficiently cool, is covered by mineral oil, to be afterwards melted in iron pots heated by an oil bath, and cast into ingots.

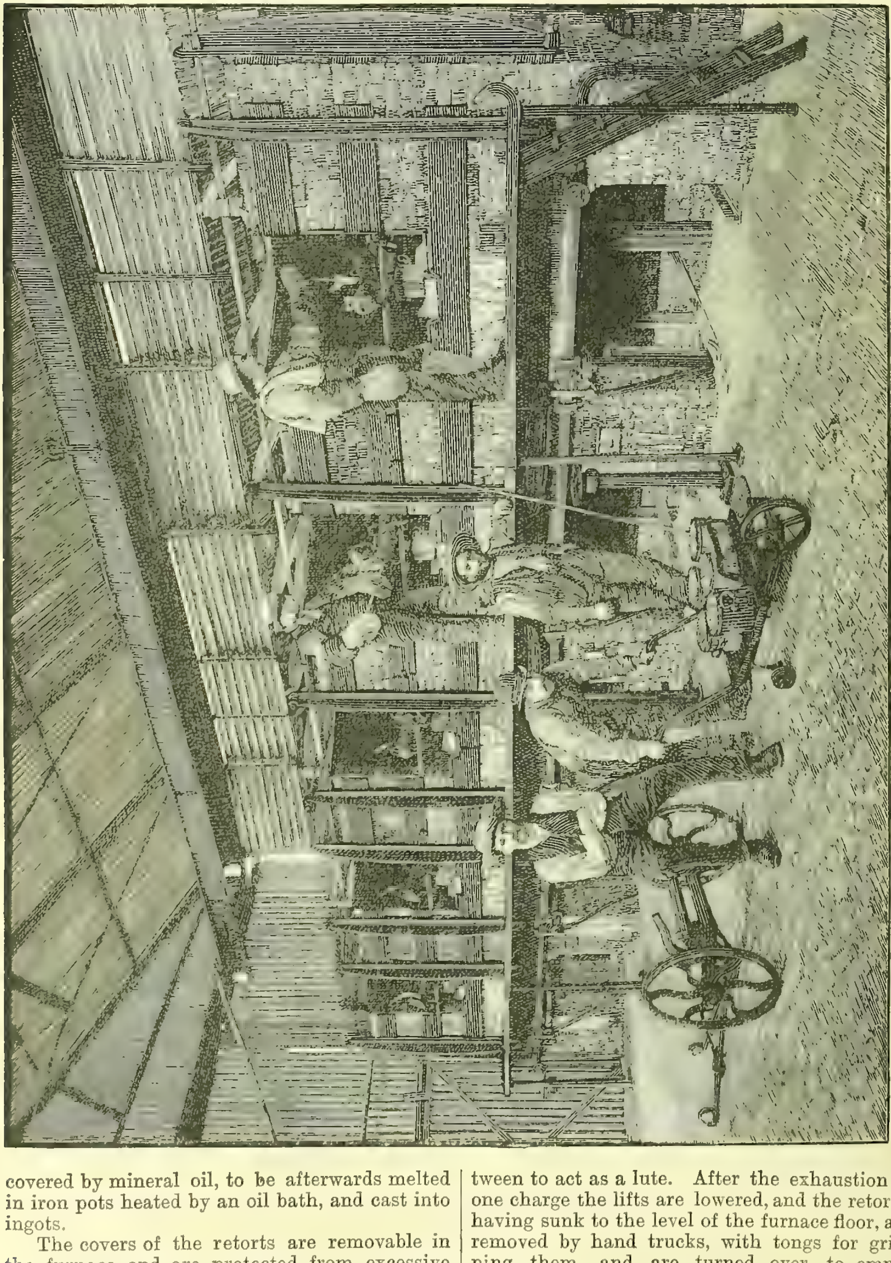

Fig. 4.

The covers of the retorts are removable in the furnace, and are protected from excessive heat by the oven setting. The body of each retort rests on a hydraulic lift and is pressed against the cover, a little lime being placed between to act as a lute. After the exhaustion of one charge the lifts are lowered, and the retorts, having sunk to the level of the furnace floor, are removed by hand trucks, with tongs for gripping them, and are turned over, to empty them into the 'dumping pits,' being then scraped clean and returned, while still red hot, to the furnace, a portion of the fresh charge being inserted on the way. A complete cycle of operations requires $1\frac{1}{4}$ hours, each retort yielding about 6 pounds of sodium.

The temperature required for the reduction is said to be about 823°, but is usually maintained at about 1000°.

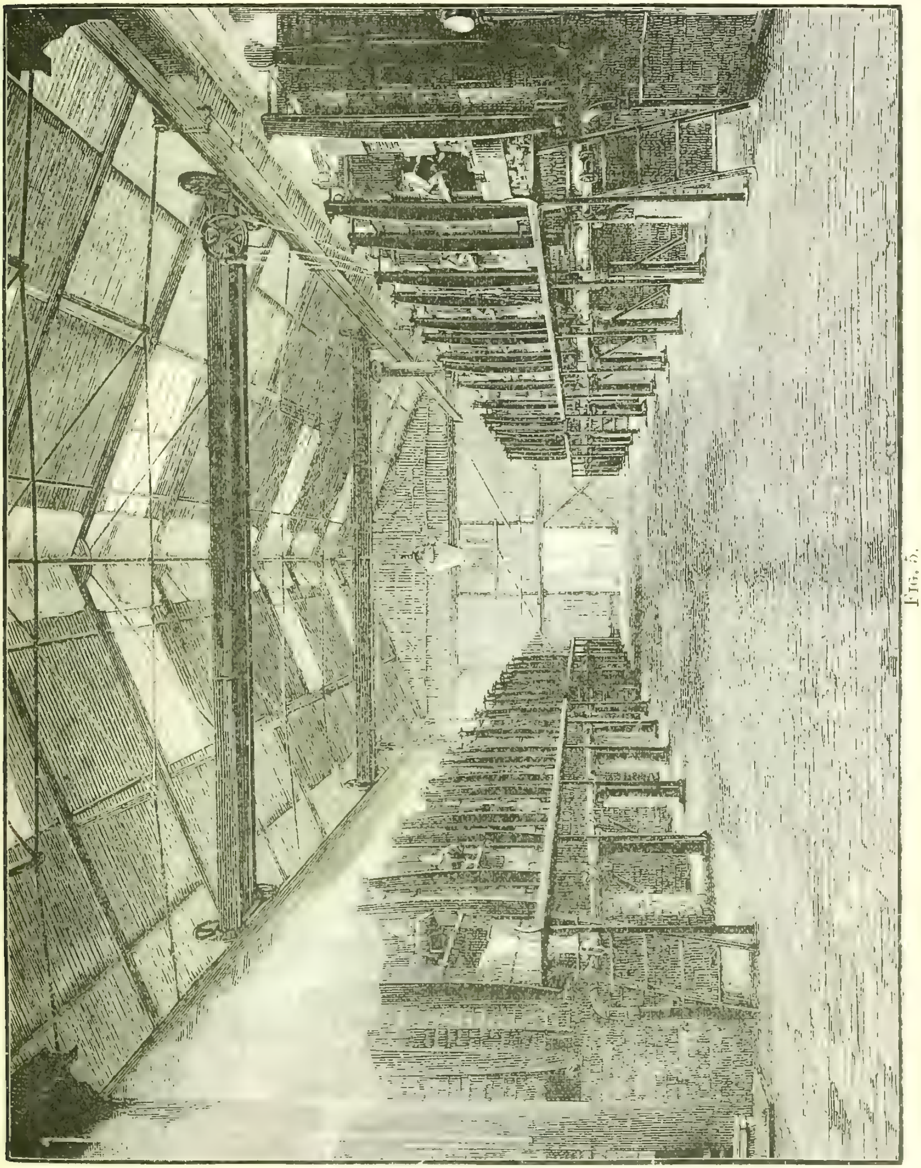

Fig. 5.

The gas evolved at the commencement of the reaction consists of almost pure hydrogen, and even at the end of the reaction only contains about 5 p.c. of carbon monoxide, which seldom combines with the sodium. When potassium is made less carbon is employed than is required by the above equation, whereby the formation of carbon monoxide is found to be altogether avoided. The residue in the retorts, which has the composition Na_2CO_3 77, Na_2O_2 2, C 2, Fe 19, is re-causticised and used again, the iron being also again employed. Figs. 4 and 5 represent the Castner plant.

For further information on the manufacture of sodium *v.* Weldon (S. C. I. 1883, 368), Fischer (D. P. J. 251, 418), Wurtz (Hoffmann's Ber. über die Entwickelung der chem. Ind. 1, 658); and regarding Castner's process *v.* Castner (*Justice*), Eng. Pat. No. 7,395 H.D. 1886, and C. N. 54, 208; Mactear (S. C. I. 1887, 174); Roscoe (P. R. I. 1889, 453, and S. C. I. 1889, 463); Anderson (J. S. Arts, 1889, 380).

The following is a list, together with an indication of the improvements claimed, of accepted patents for the preparation of sodium and potassium:—

J. Dickson, Pàt. No. 2,266, 1862 (electrolysis of the fused chloride); E. Sonstadt, Pat. No. 1,763, 1863 (replacement of the chalk or lime in the ordinary process by gypsum); J. Anderson, Pat. No. 2,801, 1867; Pat. Nos. 2,134, 2,216, and 3,493, 1871; Pat. Nos. 513 and 1,089, 1872 (heating the slag obtained by the action of heated air or steam on strongly-heated minerals containing sodium and potassium as silicate with carbon in a current of highly-heated carbon monoxide); H. Larkin and W. White, Pat. Nos. 1,990 and 3,505, 1869; Pat. No. 23, 1871 (addition of oxidising agents to the mixture, to increase the temperature within the retorts; also the use of a current of hydrogen or coal-gas, to carry off the metallic vapours; the use of macerated peat instead of coal; and a modified condenser); W. Clark (D. F. Lontin), Pat. No. 473, 1875 (electrolysis by a specially-arranged current); W. Anderson Smith, Pat. No. 363, 1876 (the use of a mixture of potash or soda with pitch, and of a modified retort and condenser; also means for coating and packing the metal); W. P. Thompson, Pat. No. 2,101, 1879 (decomposition of the hydrate by fluid iron or an alloy of iron in a Bessemer converter); C. A. Faure, Pat. No. 6,058, 1882; Pat. No. 5,489, 1883 (heating the alkaline compound in a furnace with the aid of an electric current in hydrogen or nitrogen; vessels of compressed magnesia are used); A. L. Nolf, Pat. No. 4,349, 1882 (electrolysis of a strong solution of the chloride, using a cathode of mercury); F. P. Harned, Germ. Pat. No. 26,961, 1883 (modification of the mixture used); E. A. Höffner, Germ. Pat. No. 30,377, 1884 (electrolysis of the fused chloride, using an anode of copper or silver, which takes up the chlorine); S. Gilchrist Thomas, Pat. No. 6,367, 1884 (passage of heated water-gas through the usual mixture without the aid of external heat, in retorts lined with magnesia, lime, dolomite, or graphite); H. Y. Castner (*Justice*), Pat. No. 7,395, 1886 (previously described); Max Sprenger, Germ. Pat. No. 39,554, 1886 (electrolysis of the chloride in vacuo); E. C. Kleiner-Fiertz (*Seaver*), Pat. No. 8,531, 1886 (electrolysis of cryolite or the double chloride of sodium or potassium and aluminium in a specially adapted vessel); J. B. Thompson and W. White, Pat. No. 8,426, 1887 (heating a coked mixture of alkaline carbonate and tar, or the like, in tubular fire-clay retorts containing a condensing chamber and receiver in a portion below the furnace); O. M. Thowless, Pat. No. 12,486, 1887 (the use of a mixture of separately-heated alkaline carbonate and coke); Curt. Nelto (*Lake*), Pat. Nos. 14,602 and 17,412, 1887, *v.* also Eng. and Min. J. 45, 449 (passing soda or potash in a thin stream through powerfully-heated charcoal or coke, the carbonate produced being drawn off at the bottom of the retort as produced); L. Grabau, Pat. No. 9,904, 1887 (comprises the cooling of the cathode in electrolytic processes; the metal rises to the surface, and is drawn off by a pipe); H. C. Bull, Pat. No. 10,199, 1887 (electrolytic); A. B. Cunningham, Pat. No. 3,601, 1888 (adding charcoal powder to the fused hydrate in quantity insufficient to destroy its liquidity, and decomposing the mixture in retorts); G. A. Jarvis, Pat. No. 4,842, 1888 (reduction of the fused alkali by coal, &c., and tar, or the like, coked round iron cores or in moulds; linings for the retorts are also described); W. G. Forster, Pat. Nos. 9,391, 10,785, and 14,394, 1888 (reducing the fused alkali with heated coal-gas, or like vapour); H. M. Wallis, Pat. No. 12,626, 1888 (a modification in the mixture ordinarily used); W. White, Pat. No. 13,125, 1888 (saturating lumps of charcoal with fused alkali and then heating in a retort); H. S. Blackmore, Pat. No. 15,156, 1888 (use of a mixture of lime, alkaline carbonate, ferric oxide and carbon, bitumen or like carbonaceous matter); G. M. Westman, Pat. No. 17,336, 1888 (modification of the plant treating the ordinary mixture); W. White, Pat. No. 9,784, 1889 (a modified condenser); T. Parker and A. E. Robinson, Pat. No. 11,707, 1889 (electrolysis of a mixture of the hydrate or carbonate and carbon); L. Grabau, Pat. No. 16,060, 1890 (electrolysis of the chloride, whose melting-point has been lowered by the addition of the chloride of calcium, barium, or strontium).

Properties.—Sodium has a silvery metallic lustre when freshly cut. According to Long (C. J. 13, 123), a perfectly-clean surface of the metal has a pale rose colour. It crystallises in octahedra, apparently belonging to the quadratic system (Long, *l.c.*). According to Baumhauer (B. 6, 655), its sp.gr. at 10° is 0·9743. Ramsay (C. J. 1881, 49) gives its sp.gr. at its boiling-point as 0·7414.

At $-20°$ sodium is hard, at 0° it is ductile, and at the ordinary temperature has the consistency of wax. It becomes pasty at about 50°, and melts at 95·6° (Bunsen, J. 16, 178). It boils at 861°–954° (according to Carnelley and Carleton Williams (C. J. 1879, 565); or at 742°, according to Perman (C. J. 1889, 328). Its vapour has a purple or violet colour (Roscoe and Schuster, Pr. 22, 362; Carnelley and Carleton Williams, C. J. 1879, 565). Its absorption spectrum has been examined by Roscoe and Schuster (*l.c.*).

Ramsay (C. J. 1889, 533) finds that the molecular weight of sodium, as determined by Raoult's method, varies between 15·1 and 21·6, according to the ratio between the amount of metal and solvent (mercury) used. Heycock and Neville (C. J. 1889, 666; 1890, 380) have determined the lowering of the melting-point of sodium by the presence of gold, thallium, mercury, cadmium, potassium, silver, zinc, lithium, lead, and indium; and the lowering of the melting-point of tin by the presence of sodium. Sodium is the most electro-positive element after cæsium, rubidium, and potassium, and is a powerful reducing agent; hence its use for preparing silicon, boron, magnesium, aluminium, &c., and for the reduction of gases containing oxygen, and of organic and other compounds.

It dissolves in liquefied anhydrous ammonia to a blue solution, from which it is re-obtained on evaporation of the ammonia (Seeley, C. N. 23, 169).

When exposed to the air, sodium oxidises, and ultimately becomes coated with a film of carbonate, which prevents further action. It decomposes water, with evolution of hydrogen, which does not burn unless the water be heated or be thickened with starch or the like. It burns with a bright-yellow flame when heated, with production of the monoxide and dioxide.

The halogens do not act so readily on sodium as on potassium. Wanklyn (C. N. 20, 271) and Cowper (C. J. 1883, 155) have shown that sodium may be shaken up at about its fusing-point with dry chlorine without combination; and Merz and Weith (B. 5, 646; 6, 1,518) and Merz and Holzmann (B. 22, 872) state that bromine is without action even at 300°, and that iodine does not affect it at 350°–360°.

Sodium combines directly with sulphur, selenium, and tellurium. It combines violently with potassium, and even decomposes phosphates at a red heat, with formation of a phosphide.

Alloys.—The alloys resemble those of potassium, and are obtained in a similar way. The more important have been described under the various metals. According to Vauten (S. C. I. 1891, 96), the zinc used for precipitating gold from solution in potassium cyanide in the cyanide process of extraction may be advantageously alloyed with 1 p.c. of sodium. The amalgam, with mercury, is largely used as a reducing agent, and for preventing the 'sickening' of mercury in gold extraction. The amalgams may be prepared by carefully triturating the metals together, or by adding the sodium in small pieces at intervals to gently warmed mercury. Mühlhäuser (Zeit. Chem. Pharm. 1864, 720) passes the mercury in a fine stream into sodium, heated to 90° under naphtha.

When the amalgam contains 1 part of sodium to 100 of mercury, it is liquid; but with 1 to 60 it forms a stiff paste at 21° (Böttger, J. pr. 3, 283). With less mercury the amalgam is hard and more or less crystalline. Sodium amalgam decomposes salts of the alkaline earths and of many heavy metals in presence of a small quantity of water, giving an alloy of mercury with that metal (Böttger, *l.c.*). The melting-points of a number of the amalgams have been determined by Merz and Weith (B. 14, 1,445). Crystalline amalgams of the composition Hg_6Na (Kraut and Popp, A. 159, 188) and $HgNa_3$ (De Souza, B. 9, 1,050) have been prepared, the latter, which inflames spontaneously on exposure to the air, being obtained by heating any of the amalgams to 440° (*v.* also MERCURY).

Sodium oxides. Two oxides are known, the monoxide Na_2O, and the peroxide Na_2O_2. The grey film produced by exposure of a freshly-cut surface of the metal is said to be due to formation of a suboxide.

The monoxide is best prepared by heating caustic soda with sodium:

$$NaHO + Na = Na_2O + H,$$

or, according to Beketoff (B. 12, 856), by burning sodium in a mixture of air and oxygen, excess of sodium being used to prevent peroxidation.

It is a greyish amorphous solid of sp. gr. 2·805 (Karsten, S. 65, 394), melting at a dull-red heat, and volatilising at higher temperatures. It combines with water with violence. According to Beketoff (Bl. [2] 34, 327), it is unaffected by carbon dioxide at ordinary temperatures, but combines with incandescence at about 400°. When heated in hydrogen, it becomes converted into a mixture of metallic sodium and soda: $Na_2O + H = NaHO + Na$.

Sodium peroxide is obtained as described by Vernon Harcourt (C. J. 14, 276), to whom our knowledge of this substance is principally due, by carefully cleaning and drying the metal from naphtha by gently warming it in a bulb or Florence flask in a current of nitrogen, and then displacing the nitrogen by the slow passage of dry air while gradually heating the metal up to about 200°. At that temperature the oxidation commences, and the metal becomes covered with the oxide, which rapidly increases in bulk from rise of the metal through it by capillarity and its subsequent oxidation. After the action has continued some time, the air is replaced by oxygen, which is rapidly absorbed by the monoxide, so that finally, though only after long-continued action, the whole is converted into the peroxide.

This oxide is also obtained, together with the monoxide, by igniting sodium nitrate, or by dropping sodium into molten sodium nitrate. In the latter case, the sodium burns with a bright flame and forms the peroxide, which dissolves in the nitrate to a yellowish-red solution; the colour disappears on cooling but is regained on re-heating (H. C. Bolton, C. N. 53, 289).

Sodium peroxide is of a pure white colour, but becomes yellow when heated. On exposure to air it slowly deliquesces, with ultimate production of sodium carbonate. It dissolves in water, with production of much heat and evolution of a little oxygen, probably caused by a local heating of the oxide. When added to the water in small charges very little gas is given off. On evaporation of the solution on the water bath, oxygen is evolved, slowly at first, but rapidly as concentration proceeds. Hydrates of the composition $Na_2O_2.8H_2O$ and $Na_2O_2.2H_2O$ are known (Harcourt, *l.c.*; Fairley, C. J. 1877 [1] 125).

Sodium peroxide combines with phosphorus with incandescence when heated. At temperatures above 150° it rapidly absorbs carbon monoxide, with formation of the carbonate. Carbon dioxide is similarly absorbed at about 100°, with formation of the carbonate and evolution of oxygen. When heated in nitrous oxide it produces sodium nitrite with evolution of nitrogen: $Na_2O_2 + 2N_2O = 2NaNO_2 + N_2$. With nitrogen dioxide, sodium nitrite is also produced without evolution of gas:

$$Na_2O_2 + N_2O_2 = 2NaNO_2.$$

Sodium hydroxide or **hydrate** *v.* p. 479.

Sodium chloride. *Chlorure de sodium, hydrochlorate de soude, sel marin*, Fr.; *Steinsalz, Kochsalz, Salz, Salzsaures Natrium, Chlornatrium*, Ger.; *sal*, Lat.

Sodium chloride, or common salt, is found in nature as the mineral *halite*, or *rock salt*. It crystallises in cubes, occasionally associated with other forms derived from the regular system. Hardness, 2; sp.gr. 2·2. It is colourless and transparent when pure, but is usually tinged yellow, red, brown, or green.

Owing to its wide distribution on the earth salt has been known from the very earliest times. It is frequently mentioned in the Bible. The Jewish law commanded the people to season the meat offering with salt (Lev. ii. 13). The Jews used a very impure argillaceous kind of rock salt, from which they extracted the salt by means of water, leaving the clay as mud. This mud still contained some salt, and was either used directly for agricultural purposes, or was allowed to lie on the manure heaps before being used, where, after prolonged exposure in presence of nitrogenous matter, the salt was partially converted into sodium nitrate. Hence we find the expressions (Matt. v. 13), 'Ye are the salt of the earth: but if the salt have lost its savour, wherewith shall it be salted? it is thenceforth good for nothing, but to be cast out and trodden under foot of men'; and (Luke xiv. 34) 'Salt therefore is good: but if even the salt have lost its savour, wherewith shall it be seasoned? It is fit neither for the land nor for the dunghill: men cast it out.'

Occurrence of salt.—Salt is very widely distributed. Immense deposits of it, in the form of rock salt, are found in many parts of the world. It is the principal solid constituent of sea-water and of many salt lakes, and is found in brine springs and most mineral waters. There are few countries in which it does not occur, as also there are but few geological formations from which it is absent. In America rock salt is met with in very old strata, some of the recent discoveries of it being in the Silurian rocks. In Western New York and Michigan, and also at Goderich and neighbourhood, in Canada, the rock salt is found in the Upper Silurian formation, and usually lies at a depth of over 1,000 feet. South of Rochester (New York), in what is known as the Warsaw district, the rock salt is found in three superposed beds. The top layer is 60 feet thick; then follows 10 feet of shale. The second bed is 20 feet thick, and is succeeded by 30 feet of shale. After this there is found a thick bed of rock salt, which has not yet been bored through, but it has been proved to exceed 30 feet in depth. It appears probable that the same series of deposits of salt extend eastward as far as Ithaca. The rock salt found in Michigan is principally at Saginaw, Detroit, and Bay City. In Utah there are extensive deposits embedded in red clay. Salt is also found in Virginia and Kansas. The deposits which occur in Louisiana have been known for the longest time. They lie in the Post-Tertiary formation, are from 2 to 3 miles long, and have been proved to be 38 feet thick. There are immense deposits of rock salt in Chili and Peru. Salt is found at Kulpi, in Armenia, and at Nachitschevan, in Russian Armenia. In the latter place the salt lies in the clay, and forms a nest or pocket 150 feet in diameter in red and blue marl. At Jebel Usdum, south of the Dead Sea, there is a hill which consists throughout of a single mass of rock salt, covered with a thin layer of calcareous marl. Salt is found in Algeria and Abyssinia. In the interior of Libya rock salt is found associated with limestone in cliffs. Herodotus mentions five mountains, which lie at about equal distances from one another, across a tract of country ten days' journey in extent (see H. B. Tristram, 'The Great Sahara,' p. 72). India is rich in rock salt deposits. The beds which are worked in the Punjab appear to stretch, with more or less continuity, into Afghanistan. In most places the salt is obtained by quarrying. The salt beds in Scinde are said to be 20 miles long, 15 miles broad, and 3 feet thick. On both sides of the Carpathians rock salt abounds, most of it in Tertiary formations. At Stebnick, in Galicia, the top bed lies 122 feet from the surface. At 199 feet there is a second bed of salt, 50 feet thick and very pure in quality. At 418 feet there is a third bed, which is 261 feet thick. At Wieliczka the rock salt lies in Tertiary rocks, and is found 1,200 feet from the surface. In the Tyrolean Alps rock salt occurs in Oolitic limestone, as also at Usolje, in Russia. The principal deposits in Austria are at Hall, in the Tyrol; Aussee, Ischl, and Hallstadt, in Upper Austria; Hallein, in Salzburg; and Reichenthal, in Bavaria; at Marmores, in Hungary; and in Transylvania and Wallachia. At Volterra, in Italy, there are several deposits at 150 to 308 feet from the surface. Those at Dieuze, in Lorraine, and in the surrounding neighbourhood in the east of France, are found in very thin beds, alternating with saliferous clay. In the district round Stassfurt, in Germany, immense beds of rock salt (accompanied by potassium and magnesium salts) are found in Bunter sandstone, and are first struck at about 832 feet from the surface. Salt has recently been found near Heilbronn, in the Neckar valley. At Cardona, in Spain, salt is found in the Greensand; there are hills of it 300 to 500 feet high. It has also been found at Bex, in Switzerland.

At Northwich, in Cheshire, rock salt is found in the Keuper marls, which lie interstratified with the New Red or Bunter sandstone. The top bed is about 75 feet thick, and lies 135 to 150 feet below the surface. It is covered by boulder sands, clays, and red marl. Below the top rock salt there is a bed of hard marl, 30 feet thick, which contains here and there veins of salt. Under this a second bed of rock salt is found, 105 feet thick. Deeper borings reveal the presence of successive thin beds of salt. At Winsford, in Cheshire, the beds are similarly situated to those at Northwich, and have been proved to be at least 210 feet thick. At Droitwich and Stoke Prior, in Worcestershire, the salt lies in the same formation, and is similarly accompanied by marls. At Shirley Brook, in the same county, it lies 273 feet below the surface. At the village of Preesal, near Fleetwood, in Lancashire, a bed of rock salt, 250 feet thick, is met with at a depth of 278 feet from the surface. Considerable deposits of salt have been discovered in the neighbourhood of Barrow-in-Furness. Rock salt is found at Stafford Common, in Staffordshire, 263 feet below the surface. It has also been proved to exist in the east of Lincolnshire. In the neighbourhood of Middlesbrough, in the county of Durham, rock salt has been proved to exist over an area rather more than 4 miles long by $2\frac{3}{4}$ miles broad, or 12 square miles. The most northerly bore-hole is at Grantham, where salt was found at a depth of 889 feet; the most southerly, at North Ormesby, in Yorkshire, where the bed is 1,340 feet from the surface. The most easterly bore-hole is at Eston, 1,563 feet deep; the most westerly at Haverton Hill, 797 feet deep. The average thickness of the main bed of rock salt is 84 feet. It lies below a thick bed of red sandstone.

Origin of rock-salt deposits.—The great variability in the position of the salt deposits renders it impossible to consider them as constituting a definite geological formation, but points to the probability that their origin is due either to volcanic action or to the evaporation of water which held the salt in solution. The great argument in favour of an igneous origin rests upon the fact that sodium chloride and hydrochloric acid are emitted by volcanoes; but the occurrence of layers of bitumen and certain organic remains, together with the fact that cavities containing liquids are found in the rock salt, renders this theory untenable.

The general character of the beds, too, favours the assumption that they are of aqueous origin. They are rarely found filling cavities or dykes after the manner of volcanic rocks, but are in layers of very considerable area. These immense beds of rock salt most probably owe their origin to the evaporation of inland seas, and a careful examination of their constitution affords evidence which goes far to prove this theory. The manner in which the deposits were formed appears to be as follows. When, by slow upheaval of the land or by the accumulation of a bar or sand bank, a portion of the sea became partially shut off, the heat of the sun was sufficient to evaporate as much water as was supplied by the sea or by rivers. Then the volume of water in the part so separated became gradually richer in dissolved salts. The upper layers when concentrated by the sun became specifically heavier and sank to the bottom, the more dilute rising to take their place. As the quantity of salt in solution rose, all those living organisms which were endowed with the means of locomotion left their homes and returned to the open sea, while those which were lacking in this particular died off. Their remains (such as did not dissolve) are found as insignificant impurities in the gypsum which formed around them. For by degrees the lower portion of the water became so rich in mineral constituents that it could no longer retain them in solution, and they began to separate out. The least soluble salt was, of course, the first to deposit, and this was followed by the others in the inverse order of their solubility. The calcium carbonate and ferrous carbonate, if present, would precipitate first, and then the calcium sulphate would follow in the form of gypsum. As the degree of concentration still continued to rise the sodium chloride began to separate out, depositing on the bottom of the basin in a hard compact mass. In cases where the connection with the sea was still maintained, or where rivers continued to send in water, these various phases would be to a certain extent contemporaneous; for the incoming water would bring with it fresh quantities of calcium carbonate and calcium sulphate, and these salts would precipitate along with the sodium chloride. Nor would this separation of the salts in the inverse ratio of their solubilities proceed with absolute exactitude, for the less soluble might carry down with them minute quantities of the more soluble ones. For instance, it is by no means uncommon to find magnesium sulphate mixed with rock salt, especially where there has been aluminous mud washed in to serve to carry it down. Again, certain combinations of the same salt occur, such as *simonyite*, and *bischofite* is found in solution in cavities in rock salt in Cheshire, where also *hydrophilite* is not infrequently found. As the sodium chloride continued to deposit, the mother-liquor gradually grew richer in the more soluble salts until the point was reached when they too began to crystallise. Potassium chloride and magnesium chloride separated from the solution in combination as the mineral *carnallite*. Potassium sulphate, magnesium sulphate, and magnesium chloride became associated as *kainite*, while some of the magnesium sulphate crystallised in the form of *kieserite* (*cf.* POTASSIUM, SALTS OF).

It is obvious that when the supply of fresh water from the ocean was continued at all there would be a deposit of salt accompanying the more soluble substances. The calcium sulphate, however, which precipitated from this sea water would, in falling, pass through the layers of mother-liquor which had reached a high degree of concentration; hence it crystallised as *anhydrite* (*cf.* p. 267). The whole of this process of crystallisation was, of course, subject to an immense variety of disturbing influences. The rate of deposition would vary greatly with the season of the year, not only on account of the heat of the sun and the height of the tides, but also on account of the amount of water due to the rainfall. In examining beds of rock salt we find evidences of such disturbances in the frequent occurrence of layers of clay, sandstone, or marl, which show that during certain periods there was little or no deposit of salt. In many cases the disturbance was sufficient to remove the whole of the mother-liquors, and there we find little or no trace of the potassium and magnesium salts.

Such is the generally accepted theory of the formation of the great deposits of rock salt. The ocean has for ages been receiving the waters of rivers and springs charged with matter dissolved during the passage of the water through or over the various rock formations. Such substances as were required to build up the structure of marine animals and plants were by them extracted from the water; the rest would obviously, in course of time, accumulate, because the volume of sea water was kept nearly constant by continual evaporation.

Rock salt. Rock salt is usually aggregated either in a spheroidal form or in a wavy stratification distinguishable by gradations of colour almost throughout the entire mass. The tinge of colour varies with the colour of the marl and marlstone with which it is interstratified. It varies from dark red or brown to light amber or white. The yellow rock salt is preferred, on account of its greater purity. The following table shows the composition of the salt obtained from deposits in various parts of the world.

The Cheshire salt mines which are now being worked are all in the lower bed. The rock obtained is purer than that from the upper one, and there is less trouble required to keep out surface water and brine. The modern mine is provided with two shafts placed from ten to fifteen yards apart, with generally (unless the winding shaft be tubed) another permanent shaft for pumping the surface water, sunk only

Composition of Rock Salt.

—	Cheshire	Wieliczka, white	Vic, red	Vic, grey	Hall, Tyrol	Marennes red	Virginia	Algeria	Berchtesgaden	Schwäbisc, Hall	Wilhelmsglück	Holsten, U.S.	Stassfurt	Cardona
Sodium chloride	98·3	100·00	99·80	90·30	99·43	96·78	99·55	99·30	99·85	99·63	98·36	99·55	94·57	98·55
Calcium chloride	—	—	—	—	·25	—	trace	—	—	·09	—	—	—	·99
Magnesium chloride	·05	—	—	—	·12	·68	—	—	·15	·28	—	—	·97	·02
Sodium sulphate	—	—	—	2·00	—	—	—	—	—	—	·03	—	—	—
Calcium sulphate	1·65	—	—	5·00	·20	1·09	—	·50	—	—	·55	—	·89	·44
Magnesium sulphate	—	—	—	—	—	·60	—	—	—	—	—	—	—	—
Calcium carbonate	—	—	—	—	—	—	—	—	—	—	·52	—	—	—
Magnesium carbonate	—	—	—	—	—	—	·45	—	—	—	·13	·45	—	—
Alumina and ferric oxide	—	—	—	2·00	—	·85	—	·20	—	—	·53	—	3·35	—
Water	—	—	·20	·70	—	—	—	—	—	—	—	—	·22	—
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·12	100·00	100·00	100·00

as deep as the water penetrates. In sinking the shaft it is especially requisite to protect the rock salt at the sides from being dissolved by water. All such shafts are roofed over to keep out rain and snow, and are carefully cased down to a solid foundation below where surface water penetrates in the ground. The casing was originally made of wood; but lately this has been replaced by iron. The best method of procedure is as follows:

A solid foundation, such as is generally to be found at a certain bed of marlstone between the top and bottom beds of rock salt, is obtained, and then a ledge 12 inches wide all round is cut in it, care being taken to remove any small concretions of rock salt which may be in the marl. On this ledge a wooden ring 9 inches wide and 3 inches deep is laid, and upon it is placed an iron ring 9 inches broad and 9 inches deep; this leaves an annular space 12 inches deep and 3 inches wide all round at the back of the two rings. These rings are each made in two segments.

Between the segments of the iron ring a thin slip of wood is placed at the junction, to make it water-tight, and the annular space (which is 3 inches wide and 12 inches deep) behind the two rings is filled up with pieces of wood about 6 inches long and 3 inches square, placed vertically and as close together as possible. Wedges are then driven in between the pieces of wood, and they are wedged again and again into holes made by steel points, until all is tight and the slip of wood between the iron segments becomes squeezed to a thin film. On the iron ring, which is the upper one of the two thus wedged, there is laid a thin slip of wood for the iron tubing or casing to begin upon. The bottom length of tubing is 6 feet long and is in three segments, which, when united, taper from a diameter of about 4 or 5 feet at the bottom to 3½ at the top, and on this begin the iron cylinders or tubes, which are each 6 feet long by 3½ feet in diameter. The cylinders are bolted together by means of ½-inch wrought-iron rods, which pass through four 'snugs,' or wider parts behind, on the top and bottom flanges of each cylinder, with two holes in each snug. Each bolt has a screw for a nut above the top snugs, and an eye for a cotter below the bottom snugs, and also a shoulder to prevent the rod dropping through the bottom snug-hole before the screw-nut is put on the top. The cylinders are put in from bottom to top one after another, and as the cotter cannot be put in after a cylinder is placed, the rods for bolting each upper cylinder in its turn have to be put into the snug-holes first. The cylinders have faced flanges, and the joints are made with ⅜-inch indiarubber rings, 1½ inch broad. The space behind the cylinders is filled with cement.

In the bottom bed workings the height of the rock salt that is being worked varies from 15 to 18 feet in Cheshire, and from 30 to 40 feet at Carrickfergus. The mode of working the mines in both districts is to drive out in the upper part about 5 feet 9 inches high, which is called the 'roofing,' and to follow up with what is called the 'benching,' leaving pillars of rock salt to support the roof. In driving the roofing a little holing and cutting has to be done with a pick, and as much as possible is blown out with gunpowder, after which the roof is dressed off with a pick. The benching in Cheshire varies from 9 feet 3 inches to 12 feet 3 inches in thickness, and in Ireland from 24 feet 3 inches to 34 feet 3 inches. This is blown off by a succession of shots, arranged in a slanting direction from the top to the bottom. In some of the mines machines are used. In charging the shot the fine rock salt made in drilling the hole is put next to the powder and coarse-grained rock salt upon that. The stemmers and prickers are all made of iron, as rock salt does not strike a light with iron or steel.

Flat hemp ropes are generally used for winding. In some cases iron-wire rope is used, but it has to be kept well greased to prevent it rusting. Tram roads are used below ground. It is found by experience that the pillars which are left to support the roof should be in proportion to the depth of the mine. At a depth of 330 feet it is found necessary to leave 1 pillar for every 11¼ times its area of rock worked. The pillars are left 10 yards square, and stand 25 yards apart. There is a crushing and grinding mill at the bank of nearly every rock-salt pit, and in this the rock is ground to more or less fine powder when so required for shipment.

In 1890 there were four mines being worked in England (all in Cheshire), and three in Ireland (at Carrickfergus). The amount of rock salt produced by them during the nine years ending 1890 was—

Year	Tons
1882	204,053
1883	233,170
1884	197,521
1885	190,480
1886	173,448
1887	180,422
1888	217,456
1889	161,205
1890	188,730
Total for 9 years	1,746,485
Average	194,054

Of this quantity about 20,000 tons per annum are yielded by the Irish mines.

The rock salt which is found in the neighbourhood of Stassfurt, in Prussia, is accompanied by deposits of a great variety of other minerals, especially those rich in potassium and magnesium. After boring through the Bunter sandstone, a bed of red clay and gypsum is encountered, under which lies the upper layer of rock salt, varying in thickness from 150 to 300 feet. For particulars of Stassfurt deposits *v.* Potassium, salts of.

The salt deposits in the districts of Tarapaca and Atacama, in Chili and Peru, in great measure resemble those of Stassfurt. There is, however, one remarkable point of difference—the Peruvian beds contain large quantities of sodium nitrate or Chili saltpetre. The source of this nitrogen has long been a matter for discussion; but recent researches afford most probable explanations of its origin. It is noticeable that all these 'calichales' or 'salitrales,' as the spots are called where the 'caliche' or impure soda saltpetre is found, lie near to the coast, just inside the low-lying coast Cordilleras. The coast in this part of Chili is studded with small islands containing deposits of guano rich in ammonia, and this (in the form of very fine dust) is carried by the prevailing west wind far inland, and would doubtless fall into the saline lakes when in process of evaporation. Prolonged exposure to the air at a warm temperature would cause the ammonia to become oxidised. This, taking place in the presence of a sodium salt (presumably carbonate), would give rise to the formation of sodium nitrate. The greater prominence of the more soluble potassium and magnesium salts in the nitre-bearing Chilian deposits furthers the supposition that they were formed from mother-liquors decanted from salt lakes further inland by volcanic upheaval. The theory that these mother-liquors, running down to the sea, were intercepted by the coast mountains is borne out by the fact that where there are no hills along the shore there are no nitre beds.

The manufacture of salt from sea-water.

In Portugal and certain countries along the shores of the Mediterranean, sea-water is used as a source of salt. It is evaporated by means of the sun's heat in what are called 'salt gardens.' They are large, shallow basins excavated along the seashore, consisting of (*a*) a large reservoir several feet deep, into which the sea-water is drawn at high tide through a sluice (this pit is used to allow the water to deposit all suspended matter before being run off into the evaporating pans); (*b*) the crystallising pits. These are very shallow basins through which the brine is made to flow in a zigzag course. They cover some acres of ground, and are well exposed to the action of the winds. The sea-water is let into the settling reservoir in the month of March, and the crystallising pans are fed from this as they get low. The salt is raked out from time to time, and allowed to stand to drain. In some parts it is stacked until the magnesium chloride which it contains absorbs moisture and runs away. The mother-liquors, technically termed 'bitters' or 'bittern,' are allowed to run back to the sea, or are used for the manufacture of bromine. They are comparatively rich in magnesium and calcium bromides. In some cold countries, such as Russia and Sweden, the reverse process is employed to obtain salt from sea-water. The salt water is allowed to freeze, and the ice, which consists of nearly pure water, is removed. By repeating this several times a mother-liquor is obtained which is sufficiently strong to boil down. The salt obtained in this manner is far from pure. It contains from 75 to 85 p.c. of sodium chloride.

Manufacture of salt from brine.

The manufacture of salt has been carried on in England since the time of the Romans, who, there is little doubt, made it from brine. Brine is formed by fresh water reaching the surface of the rock salt, either at the outcrop of the strata or through a fissure in the overlying marl. In Cheshire it is pretty certain that the water gains admission at a higher level than the rock salt, for when the brine is first struck it rises up the shaft to a considerable height, in some cases nearly to the surface. The brine is, as would be supposed, only found on the top of the upper beds of rock salt. It is reached by sinking a huge well or shaft, sometimes as much as ten feet in diameter. For the purpose of keeping water out, the shaft is lined with cast-iron cylinders carefully jointed together (see description of rock-salt mine shaft), or with timber backed with puddle. This shaft is carried down until the marl is reached, and then a bore-hole is driven until the brine is tapped. The top bed of rock salt in Cheshire is usually covered with a bed of marlstone, locally called 'the flag,' which is very hard and impervious to water. For a few feet below the flag the marl in which the rock head brine runs is of a granular structure, locally known as 'horse beans' or 'shaggy metal,' and is probably the remains of marl or other impurity originally combined with the rock salt, but left behind as the rock salt is dissolved into brine. On piercing the flag the brine rises into the shaft with great force. Common lift pumps are employed to raise the brine to the surface. They are suspended by a chain of rods depending from a rocking shaft or T-bob at the top of the well. One engine, placed near the top of the shaft, generally works a pair of pumps. The brine is delivered into reservoirs which are lined with puddle-clay and brickwork. The clay suffices to make them watertight, and the bricks, which are laid on the top of the puddle, keep it from being washed out. The brine is distributed to the salt-pans through pipes. In Cheshire it is customary to employ pipes made out of the trunk of a tree bored out in the core and tapered at one end. The taper end fits into the core of the next pipe. Such ranges are found to stand changes of temperature better than iron ones. In Austria also there are many miles of such ranges of pipes. The brine used at Ebensee is conveyed from Hallstadt. The strength of brine varies very greatly. It is, of course, dependent upon the volume of water which passes over the rock salt, the area of the surface over which it runs, and the length of time it is in contact with it. The table on this page shows the composition of brine in various places and countries.

In some countries where the brine is found too weak to make the ordinary method of evaporation a profitable one, recourse is had to a device to strengthen the brine by evaporation at the ordinary temperature. This is done by means of so-called graduation towers or houses (German, *Gradirhäuser*). They consist of scaffolding which incloses bundles of brambles or thorns, built up in regular walls. The weak brine is pumped up to the top, and carefully distributed by means of perforated troughs all over the summit of the pile. It then falls from twig to twig, and is divided into a fine shower on its way to the ground, thus exposing an immense surface to the action of the air or wind. At the bottom it falls into a collecting trough, whence it is returned to the top of the same or another tower until it becomes sufficiently concentrated. In time, the thorns become coated with a scale of calcium carbonate and sulphate, and then they have to be renewed. This incrustation is technically known as thorn-stone (German, *Dornenstein*). The graduation houses should be built lengthwise in the direction of the prevailing wind. The rapidity of evaporation

Composition of brines.

100 parts of brine contain	Marston	Wheelock	Droitwich	Stoke Prior	Friedrichshall	Hall	Artern	New York, Salina	Alleghany Mountains	Nauheim	Homburg	Moutiers	Schönbeck	Clemenshall	Sulz	Dürrenberg	Rodenberg	Syracuse, New York, U.S.A.
Sodium chloride	25·222	25·333	22·452	25·492	25·563	25·717	25·267	13·239	3·200	2·730	1·600	1·058	9·623	25·902	23·473	6·599	5·173	21·71
Potassium chloride	—	—	—	—	—	—	·119	—	—	—	·003	—	·007	—	—	·008	—	—
Magnesium chloride	—	·171	—	—	·005	—	·421	·046	·293	·265	·130	·030	·083	—	—	·092	·166	·136
Calcium chloride	—	—	—	—	—	—	—	·083	·568		—	—	—	—	—	—	—	·188
Potassium sulphate	—	—	—	—	—	—	·291	—	—	—	—	—	·014	—	—	·004	·515	—
Calcium sulphate	·391	·418	·387	·261	·437	·171	·400	·569	—	·005	·002	·251	·339	·444	·508	·250	—	·505
Sodium sulphate	·146	—	·390	·594	—	·038	—	—	—	—	—	·100	·249	·019	—	·208	·005	—
Magnesium sulphate	—	—	—	—	·023	—	—	—	—	—	—	·055	·012	—	—	·004	·010	—
Calcium carbonate	—	·052	—	—	·010	·002	—	·014	—	·128	·102	·076	·026	·019	·016	·026	—	—
Magnesium carbonate	·107	·107	·034	·034	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ferrous carbonate	—	—	—	—	—	—	—	·002	—	·001	·009	·012	·001	—	—	·004	—	·005
Silica	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Organic matter	—	—	—	—	—	—	—	—	—	—	—	·001	—	—	—	·012	—	—
Total	25·866	26·081	23·263	26·381	26·038	25·928	26·498	13·953	4·061	3·129	1·846	1·583	10·354	26·384	23·997	7·207	5·869	22·545

depends upon the hygrometric state of the atmosphere. On rainy days graduation cannot go on. Experience shows that from May to August is the best season. It has been calculated that in ordinary good weather 60 kilograms (13 gallons) of water are evaporated in the course of twenty-four hours for every square foot of surface of the thorns. This method of evaporation is employed among other places at Moutiers in France, and at Nauheim, Dürrenberg, Rodenberg, and Schönbeck, in Germany.

In some districts where rock salt is found the water does not naturally percolate to the strata, and therefore no brine is struck when borings are made. An artificial brine is readily prepared by turning a stream of fresh water down on to the bed of salt, and then pumping it up again as it becomes saturated with salt. The strong brine, being much heavier than water, collects at the bottom of the shaft; so the pumps are made to draw from the bottom, and are only run so long as the brine delivered keeps up to strength. The yield of such a brine shaft, of course, depends upon the area of the surface of the rock salt which the water can act upon, and this it will be seen is always increasing. The whole of the brine evaporated in the Middlesbrough district is made in this way. Water from the sandstone strata is allowed to flow down the well outside the pump barrels, and thus solution of the salt takes place at the top of the bed, by which a cavity is formed. As the brine is pumped from the bottom of the cavity more water flows down, and thus the cavity becomes larger and its productive power is increased. As the specific gravity of brine is about 1·2, the column inside the suction pipe rises to $\frac{5}{6}$ of the height of the water column outside.

The removal of these subterranean beds of rock salt by the agency of water occasions in some districts very serious consequences. In carefully worked mines the pillars which are left are ample to support the superincumbent strata so long as the mine is kept dry. But if, by any chance, water finds its way in large quantities into a salt mine the pillars are rapidly dissolved, and a large area of roof is left without any support. Then a subsidence of the land, occurring more or less rapidly, is sure to take place. The water which finds its way down to the rock-salt beds may run for miles along its surface, and so gradually remove an ever-increasing layer of the salt. If there is no natural outlet the solution of salt ceases when the water becomes saturated; but if the brine is pumped out for manufacturing purposes an equivalent volume of fresh water is induced to flow in, and so the destruction of the salt bed is greatly intensified. This constant removal of the support causes as constant a subsidence of the outlying lands, and it is by no means uncommon in the brine-pumping districts for pieces of land to sink at the rate of a foot a year. In the Middlesbrough district, however, no subsidence has yet been observed. One would not expect to find any except in the immediate vicinity of the brine wells, because it is only there that solution of the rock takes place. Then, too, the enormous thickness of the sandstone (500–600 feet) lying over the rock salt is amply sufficient to form a strong arch over the cavities and prevent the surface from sinking.

The process employed for manufacturing salt from brine is extremely simple. It merely consists in the evaporation of the water and the collection of the salt which deposits. It is obvious, therefore, that the best process is that which secures the greatest evaporation for the smallest expenditure of heat. Although, in England, the manufacture of salt has been carried on since the Roman occupation, the process has undergone so little change that the plant in use to-day is not essentially different from that employed fourteen hundred years ago. During the last two hundred years some hundreds of patents have been taken out, but the improvements were of such doubtful utility that not one of them has been generally adopted. The following is a list of some of the most important of the patents:—

In 1764 John Baker patented a salt-pan covered over from end to end with a brickwork arch, and so arranged that the hot gases which had already passed under the pan should be drawn over the surface of the brine.

In 1772 Daniel Scott and John Mackay proposed to arrange pans three high, and conduct the steam from the bottom boiling pan through false bottoms under the other two.

In 1801 James Manly patented a process for purifying brine. He proposed to heat, in order to remove part of the impurity, and then to add carbonate of soda to it.

In 1806 Richard Tomkinson designed a salt-pan which contained a hollow iron cylinder running right down the centre and out at the other end. The middle of the pan was deeper than the sides, and the cylinder was supported so that the brine surrounded it at all times. The fire was placed in the cylinder at one end of the pan.

In 1808 William Steel patented a plant consisting of three separate vessels. The boiling vessel was provided with an air-tight cover, and the steam from it was conducted under a second vessel. The hot air and flame from the flue of the first was taken under a third vessel.

In 1824 W. A. Jump and W. Court proposed to heat the first brine in metallic pipes, placed in the flues under the pan.

In 1831 W. A. Jump patented a pan provided with mechanical rakes to draw the salt to the side of the pan.

In 1833 W. Newton proposed to blow hot air through the evaporating brine.

In 1838 Joseph Hall patented a circular revolving pan. The salt, as it formed, was scraped by means of a fixed rake into a pocket at the circumference of the pan. He also described a semicircular pan with a reciprocating motion. He claimed that in such pans the heat was more evenly distributed and the wear consequently less.

In 1839 Edward Law patented a machine for evaporating brine by exposing an extensive surface to the action of a brisk current of air. The apparatus consisted of an upright shaft or axis carrying ten frames covered with canvas. These were constantly moistened with brine while the machine was turned rapidly on pivots.

In the same year (July 16, 1839, No. 8155) an important step was taken by John Reynolds, who invented a process for improving the manufacture of salt by 'causing the steam produced by boiling brine or salt water in a closed vessel to transfer its heat to and thereby boil brine or salt water in a second closed vessel, so that the steam from such second closed vessel may in like manner transfer its heat to brine in a third vessel, and so on, by maintaining in each of a series of closed vessels in which brine is subjected to evaporation such relative pressure as will cause the respective boiling-points of the brine contained in each to be lower from the first to the last of the series, so that the steam or vapour produced from the brine in each vessel may be condensed in a vessel of thin metal immersed in the brine of the next succeeding vessel. The graduations of pressure may be obtained either by diminishing a pressure superadded to that of the atmosphere, or by diminishing the pressure of the atmosphere alone.'

In 1855 L. J. F. Margueritte proposed to precipitate salt from a solution by passing hydrochloric acid gas into it.

In 1864 D. Hall and A. L. Roosen patented the application of surface heating for the evaporation of brine. The pan was covered with a brick arch, and the heat from the furnace was allowed to pass over the surface of the brine, and then afterwards, together with the steam evolved, under an ordinary open salt-pan.

Of late years the greatest improvements which have been made in the manufacture of salt have been in the direction of the triple effect apparatus described by Reynolds in 1839. The cost of fuel is so large an item in the cost of production of salt that any economy effected in its use materially increases the margin of profit. With the ordinary open pans one ton of fuel (containing 80 to 85 p.c. combustible matter) will make from 2 to 2·2 tons of salt. A well-constructed triple effect plant will make four tons of salt for one ton of fuel. The process consists essentially in the utilisation of the latent heat of the steam in connection with the lowering of the boiling-point, by employing a pressure below the atmospheric one. In such a way a liquor which has a high boiling-point is energetically evaporated by means of the ordinary exhaust steam from engines, and the steam yielded by evaporation is used over again for the evaporation of another portion of the liquor.

The ordinary process of manufacturing salt from brine is as follows: the brine is run into a shallow pan, which is heated from below, and is made of such a shape as will expose as much surface as possible both to the action of the fire and of the air. The oldest pans of which there is any record were made of sheet lead, and were only about 3 feet square and 3 to 4 inches deep, holding little more than 15 gallons. These so-called 'leads,' when filled, were set aside in a warm place or on a hot flue, until the brine deposited its salt. About the middle of the seventeenth century iron pans superseded the leaden ones, and these were constantly made larger in size. In 1765 the largest pans used at Northwich were 20 feet long by 9 or 10 feet wide. At the present time the smallest employed are 25 feet long by 20 feet wide and 15 inches deep, while some of the pans used for making coarse salt are 70 feet long by 25 feet wide and 18 inches deep.

The pans are placed upon brickwork, which serves for a support and also forms the walls of the flues. The fireplaces are placed in the front, and vary in number from 2 to 4, according to the size of the pan and the work it has to do. The flues are frequently carried straight from front to back of the pan. In some pans the portions marked F in figs. 7 and 9 are shut off from the flues in order that when the salt is raked up to the side, previous to drawing, it does not cause super-heating of the pan plates. Fig. 6 shows the front view of a salt-pan; fig. 7 is a cross section at the break shown in fig. 8; fig. 8 is a longitudinal section; fig. 9 is a plan of the flues.

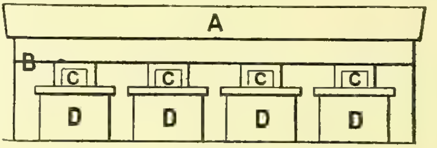

FIG. 6.—SETTING OF SALT-PANS.

A. The salt-pan. B. The front wall or fore-bye. C, C, C, C. The fireplaces. D, D, D, D. Ash holes.

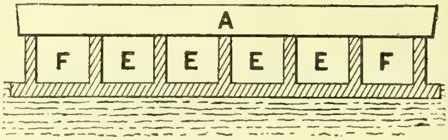

FIG. 7.—SETTING OF SALT-PANS.

A. The salt-pan. E, E, E, E. The flues.

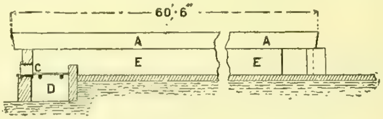

FIG. 8.—SETTING OF SALT-PANS.

A. The salt-pan. C. Fireplace. D. Ash hole. E. Flue.

The pans are made of wrought-iron plates carefully riveted together like boilers. The plates which lie directly over the fires are made of greater strength than the rest of the pan, on account of the greater wear which they have to stand. As the plates have to be renewed more frequently than any others, they are made smaller, and are so arranged that they can readily be cut out (see fig. 10). Each set of fire-plates A, A, A, A, is separated from its neighbours by

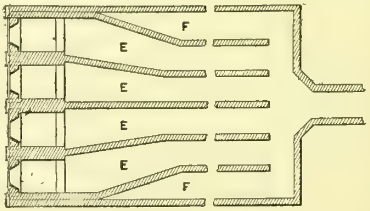

FIG. 9.—SETTING OF SALT-PANS.

E. Flues. F. Blank space.

a midfeather plate BB, which rests upon the wall dividing two fireplaces. The two outer sets are separated from the side of the pan by a similar long plate. The bottom and sides of the pan are joined by means of an angle iron, to which each is firmly riveted (fig. 11).

As above stated, the plates A which lie in the vicinity of the fires are subjected to the greatest wear. When they become over-heated they sink and stretch, and, in so stretching, they tear the plates C at the front of the pan. It is obvious that the removal of the front plate would necessitate frequent interference with the angle iron, and this would entail a greater expenditure of labour; therefore it is found advisable to place two rows of plates along the front. All the plates used in the neighbourhood of the fires are $\frac{3}{8}$ inch thick, while those employed for the back parts are $\frac{1}{4}$ inch. Some French pans have the fire-plates raised towards the centre above the level of the rest of the pan (see fig. 14), in order that the salt, when formed, may float off the fire-plates. Salt pans should be made to extend about 1 foot or 1 foot 6 inches beyond the front wall, in order to keep the angle iron well out of the fires. They are also made to overlap the side walls by about 6 inches, for the double purpose of keeping the angle iron clear of the flues, and for allowing what is known as toe-room for the man who draws the salt out of the pan. If the drawer can place his toe under the pan, he is able to get his leg flat against the side of the pan. This affords him greater power in stooping over the pan, and prevents him wearing the skin off his knee. The best method of setting the pan on the side walls is to build up a 9-inch wall, and make the top course of bricks only $4\frac{1}{2}$ inches (see fig. 12).

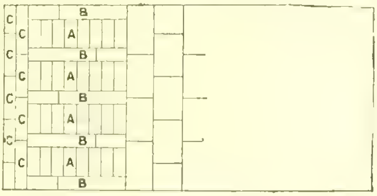

Fig. 10.—Plan of Salt-pan, showing Arrangement of Plates.

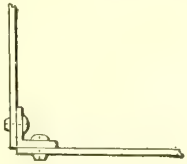

Fig. 11.

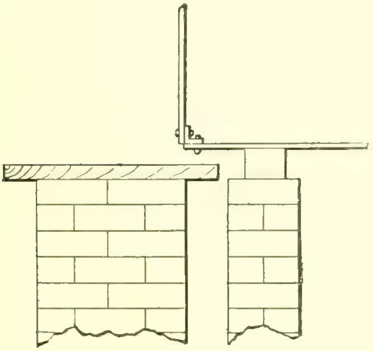

Fig. 12.

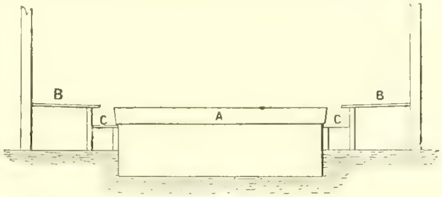

Fig. 13.

A. Salt-pan. B, B. The hurdles. C. Standing side.

What is technically known as the 'standing side' consists of a gangway of 2-inch planks about 2 feet wide, which runs the entire length of the pan, on a level with the top of the 9-inch side wall. On both sides of the pan, and often across the back, there runs a platform composed of 2-inch planks well jointed together, and caulked with oakum. These stages are technically known as the 'hurdles,' and serve for a receptacle for the wet salt freshly drawn from the pan. They have a fall towards the centre or half-length of the pan, and are bordered on the pan side by a gutter in order that the brine which drains from the salt may run back into the pan. It is customary on the Continent to cover in the salt-pans with a wooden shelter, provided with an upright shoot to take off the steam. In such cases this cover serves instead of the hurdles, and it possesses the distinct advantage that the heat from the pan serves in a great measure to dry the salt. In some Continental works a tramway runs down the centre of this wooden cover, and the salt is taken off in trucks (see figs. 14 and 15).

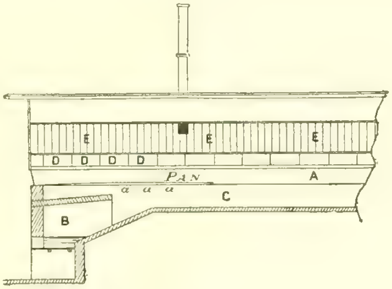

Fig. 14.—Longitudinal Section of a French Salt-pan, showing Shape of Pan and Arrangement of Wooden Cover.

A. Salt-pan. *a, a, a.* Raised fire-plates. B. Fireplace. C. Flue. D, D, D, &c. Movable doors in cover. E, E, E. Cover forming hurdles.

Fine-grained or lump salt. Fine-grained salt is made in the smallest-sized pans. These are 25 to 35 feet long and 20 to 24 feet wide, and 15 to 18 inches deep. The brine is boiled and reaches the temperature of 226°F. or 107·5°C. As the salt forms it is raked off the fire-plates to the side of the pan from time to time. Twice or three times in twenty-four hours the salt is drawn from the pan.

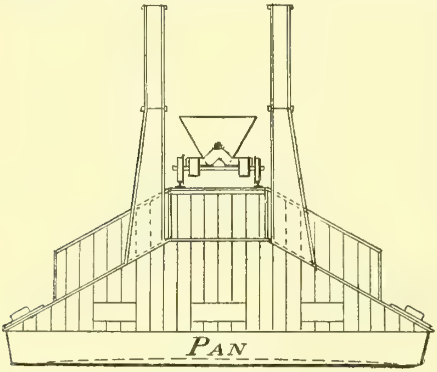

Fig. 15.—Front View of a French Salt-pan, showing Chimneys to carry off the Steam.

Dotted line shows curve of the pan over the fires.

The salt is lifted out of the pan on a perforated sort of shovel, known as a 'skimmer' (fig. 16). As it is drawn out of the pan it is placed either in wooden boxes (fig. 17) standing on the hurdles, or thrown on to the hurdles in bulk. As it cools in the boxes the hot brine which it contains crystallises, and suffices to cement the whole together into a solid mass. This is knocked out of the box and placed in the stoving chamber to dry. This hot room is generally heated by the waste heat from the flues of boiling pans. The fine table salts are prepared by crushing and grinding the lumps after drying.

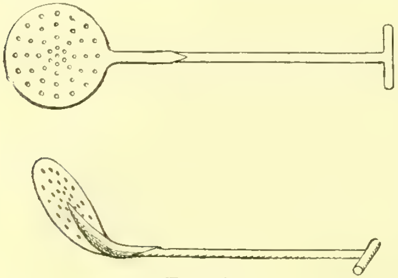

Fig. 16.

Common salt. The name 'common' is given to that grain of salt which is made for use in various manufacturing operations. It is made at a temperature of 160° to 180°F., or 61° to 82°C., in pans 45 feet long by 25 feet wide and 18 inches deep. The salt is raked off the fires about every two hours, and drawn out of the pan every twenty-four or forty-eight hours. After draining on the hurdles for some hours it is shipped off in railway waggons.

Fishing salt. Fishing salt is a coarse-grained variety manufactured for the fish-curing trade. It is made at a temperature of 100° to 140°F., or 37·7° to 60°C., in pans 50 to 60 feet long by 24 to 25 feet wide and 2 feet deep. The salt is drawn out once a week or once a fortnight, according to the grain required. These pans are often heated by the flue gases from boiling-pans.

Bay salt. Bay salt is the coarsest-grained salt manufactured. The pans employed are very large, sometimes even 140 feet long by 25 to 30 feet broad. The temperature of the brine is kept at about 100° to 120°F. The salt is drawn every three weeks or month.

The salt manufacturer frequently manipulates his brine in order to obtain the exact grain of salt that he requires. The addition of gelatin, glue, or any kind of grease causes the salt to form in very small crystals, whilst the addition of alum has the opposite effect. The operation of adding such substances is technically known as 'poisoning the pan.' Alum is employed in the manufacture of a variety of salt known as 'hopper salt.' It causes the salt to crystallise in hollow cubes, and as these float about before falling to the bottom of the pan they become surrounded by others, and gradually form into the shape of a shoot or hopper (fig. 18).

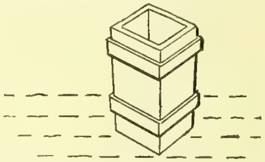

Fig. 17.—A Box for Lump Salt.

Natural brine is seldom a solution of pure sodium chloride, but generally contains other salts in solution, as will be seen from the foregoing analyses (p. 432). Certain of these substances separate out during the process of evaporation, and not only render the salt impure, but give trouble in the pan. If the brine contains calcium bicarbonate, the application of heat produces a precipitation of calcium carbonate. When this occurs in a salt-pan the carbonate of lime (which is almost always accompanied by oxide of iron) deposits on the top of the fire plates, and forms what is technically called 'sand scale.' This has to be broken from time to time with a blunt pick and fished out of the pan, otherwise the plates would get red hot and burn away. When a pan begins to leak, the brine often crystallises as it drops into the flue, and forms a stalactitic mass, which is locally called a 'cat.' This is not the only trouble caused by a leaky pan, for, in addition, hydrochloric acid is frequently formed, through the decomposition of sodium chloride by sulphur dioxide in the presence of water. The sulphurous acid is generated by the combustion of small quantities of pyrites in the fuel. All British salt works are now under Government

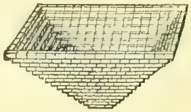

Fig. 18.

inspection, and the chimney gases are tested from time to time by the inspectors.

If brine contains calcium sulphate, it deposits it when heated. This falls to the bottom of the pan, and forms a scale which frequently contains a large quantity of salt. It sometimes accumulates to a thickness of 4 inches and is known as 'pan scale.' On account of the growth of scale and the consequent decreased efficiency of the pan, it becomes necessary after working for a given time to run off all the liquid from the pan and remove the scale. This operation is termed 'picking' the pan.

In the Warsaw district, and at Syracuse and other places in New York State, U.S.A., brine is evaporated in small cast-iron pans shaped like basins, and locally known as 'kettles.' They are about 4 feet diameter and 2 feet deep. They are set in rows on the top of a long flue. A basket is placed on two iron rods which rest on the rim of each pan, and the salt when drawn is thrown into the basket and allowed to drain into the pan.

In the same districts large quantities of salt are made by solar evaporation. The pans are made of wood and rest upon the ground. They are usually 18 feet long and 16 feet wide and 4 inches deep. Each pan (technically termed a 'cover') is provided with a movable roof. In fine weather this is pushed on one side, and the brine is exposed to the rays of the sun. During rain it serves to keep the salt from being re-dissolved.

Along the banks of the Yang-tze river in China there are numerous wells from which brine is extracted in bamboo pipes, and then evaporated by means of gas from adjacent petroleum wells. A large quantity of salt is made at Tzu-lin-ching. A well of so-called 'black' brine will yield about three tons of salt per day.

In India large quantities of salt are made by solar evaporation. The manufacture is only carried on during the hot rainless season. The brine is run into shallow ponds, which cover very large areas. Along the Coromandel coast there are numerous salt-gardens where sea-water is evaporated. In Madras and Orissa alone there were 69 factories at work in 1889. In the Scinde district the principal works are at Maurypur, where there are 59 in operation. In the Gwalior district brine is made from saline soil and then evaporated by the sun's heat.

Statistics of the manufacture and export of salt. United Kingdom.

The salt which is produced in the United Kingdom consists of rock salt and white or manufactured salt. The Leblanc soda industry consumes a very large quantity of the manufactured salt; but in the ammonia soda process the salt is used in the form of brine. In the Government returns this salt is treated as salt produced under the head of 'salt in brine.' In Ireland the white salt is manufactured from rock salt, which is dissolved in sea-water when available. The following table gives the production for the United Kingdom for the last nine years:

Total white and rock salt, and salt in brine, produced in the United Kingdom.

Year	Rock salt	White salt	Total tons
1882	204,053	1,931,446	2,135,499
1883	233,170	2,092,550	2,325,720
1884	197,521	2,135,183	2,332,704
1885	190,480	2,017,203	2,207,683
1886	173,448	1,968,772	2,142,220
1887	180,422	2,013,529	2,193,951
1888	217,456	2,088,113	2,305,569
1889	161,205	1,785,291	1,946,496
1890	188,730	1,958,119	2,146,849
Totals for nine years .	1,746,485	17,990,206	19,736,691
Average per year . .	194,054	1,998,911	2,192,965

The total quantity produced in 1890 was made up from the various districts as follows:—

County	Rock salt	White salt	Total
England.	Tons	Tons	Tons
Cheshire	159,088	1,440,088	1,599,176
Durham	—	199,971	199,971
Lancashire	—	7,877	7,877
Staffordshire	—	7,135	7,135
Worcestershire . . .	—	267,348	267,348
Yorkshire	—	35,700	35,700
Totals . . .	159,088	1,958,119	2,117,207
Ireland.			
Antrim	29,642	—[1]	29,642
Totals for the United Kingdom .	188,730	1,958,119	2,146,849

[1] Quantity 14,801 tons included as rock salt.

The following table (from the Board of Customs return) shows the countries to which the British-made salt is exported:—

Country to which exported	1889		1890	
	Quantity. Tons	Value. £	Quantity. Tons	Value. £
Russia	7,946	4,389	16,123	9,225
Sweden and Norway . .	31,200	18,816	25,313	14,924
Denmark	35,685	17,976	26,213	12,235
Germany	22,839	12,023	24,672	14,556
Holland	21,248	6,385	15,835	4,571
Belgium	21,466	14,936	27,359	17,228
West Coast of Africa . .	32,241	33,584	37,340	46,000
British East Indies . .	244,385	169,438	289,983	247,361
United States of America .	119,087	130,887	113,990	128,259
Australasia	32,718	42,960	52,271	66,137
British North America . .	64,289	49,952	70,334	57,277
British West Indies . .	6,499	8,059	5,389	8,019
Foreign West Indies . .	770	551	37	77
Chili	4,583	4,385	2,795	3,490
Brazil	6,556	6,373	8,346	8,566
Other countries . . .	11,245	17,799	10,021	14,746
Totals . . .	666,757	538,513	726,021	652,671

Salt produced in British Colonies and Dependencies, 1889.

	Tons
Cape of Good Hope . .	584
Ceylon	1,450
India	1,028,813
South Australia . . .	3,286
Canada	29,314

Salt produced in Foreign Countries.

	Tons
France	747,000
Algeria	30,400
Prussia	520,000
Bavaria	43,000
Germany (other parts) .	475,000
Austria	283,000
Hungary	160,000
Italy	413,000
Russia	1,156,000
Spain	414,000
Switzerland	42,000
Greece	17,500
United States . . .	1,023,000
Japan	100

J. I. W.

Sodium bromide NaBr may be prepared similarly to the iodide (*q. v.*). Castelhaz (Am. J. Pharm. 42, 509) recommends its preparation for medicinal purposes by double decomposition between sodium carbonate and ammonium bromide.

When crystallised from solutions at temperatures above 30°, it is obtained in anhydrous cubes, but if deposited below that temperature the crystals form rhombic prisms of the composition $NaBr2H_2O$. According to Kremers (J. 1858, 41), the salt dissolves in 1·29 parts of water at 0°, and in 0·87 parts at 100°. The saturated solution boils at 121°. It dissolves in 13 parts of alcohol at 15°, and in 11 parts of boiling alcohol.

Chlorine displaces bromine from the bromide to a limited extent even at the ordinary temperatures (*v.* Potilitzin, B. 12, 695).

A body crystallising in hexagonal plates and having the composition $NaBr.2As_2O_3$ has been obtained by Rüdorff (B. 21, 3051) by dissolving arsenious oxide in a boiling solution of the bromide.

Sodium iodide NaI may be obtained in a state of purity by dissolving sodium hydrate or carbonate in hydriodic acid, or, preferably, by dissolving iodine in caustic soda until the solution is permanently brown, and evaporating the solution of mixed iodide and iodate thus obtained ($6NaHO + I_6 = 5NaI + NaIO_3 + 3H_2O$) to dryness, and heating it to dull redness to reduce the latter salt to iodide. For pharmaceutical purposes, powdered wood charcoal is usually mixed with the residue before ignition to facilitate the reduction.

It is also sometimes prepared by decomposing a solution of ferrous iodide obtained by the action of iodine on iron in presence of water, with sodium carbonate (*v.* further, Procter, Am. J. Pharm. 1854, 305). At a temperature of 20° or upwards, sodium iodide separates from solution in anhydrous cubes, but below that temperature it crystallises in deliquescent hexagonal plates of the composition $NaI.2H_2O$. Sodium iodide fuses at 628° (Carnelley, C. J. 33, 279). According to Kremers (P. 97, 14), it is soluble in 0·63 parts of water at 0° and in 0·32 parts at 100°. The saturated solution boils at 141°. A compound of sodium iodide and iodate $3NaI.2NaIO_3.20H_2O$ is said to exist (Marignac, J. 1857, 124), and Rüdorff (B. 21, 3051) has obtained crystalline plates of the composition $NaI.2As_2O_3$ by slowly cooling a solution of arsenious oxide in a boiling solution of sodium iodide.

Sodium iodide is used to some extent medicinally in place of the potassium salt.

Sodium sulphites. The normal sulphite of sodium forms anhydrous crystals of the composition Na_2SO_3, or hydrated crystals of the composition $Na_2SO_37H_2O$. It is usually prepared by passing sulphur dioxide gas through a solution of sodium carbonate or hydrate, or over crystals of the carbonate, until absorption ceases. The bisulphite $NaHSO_3$ which is thus formed is then converted into the normal salt by the addition of as much sodium carbonate as was originally present: (1) $NaHCO_3 + SO_2 = NaHSO_3 + CO_2$; (2) $2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + CO_2$.

The following method is recommended by Hartog (Brit. Assoc. Reports, 1889, 549, and C. R. 109, 179, 221, and 436) for preparing the pure normal sulphite. A solution of 300 grms. of sodium carbonate in 100 c.c. of water freed from dissolved oxygen by passing nitrogen through it, as recommended by Berthelot, is saturated with sulphur dioxide, and a concentrated solution of 300 grms. of sodium carbonate is added. The bottle being then placed in an oil bath heated to 120°, the salt rapidly deposits from the solution in small anhydrous crystals.

On the large scale, the sulphite is obtained by passing sulphur dioxide through a solution of the carbonate, or through a vessel filled with the crystals, until a sample possesses an acid reaction. The solution of sulphite and bisulphite thus obtained is heated to boiling, and treated with sodium carbonate until carbon dioxide ceases to be evolved. The liquid is then settled, decanted, and crystallised.

If the carbonate crystals or solution be kept below a temperature of 15°F., the result of the reaction is practically a mixture of the normal salt and bisulphite produced according to the above equations, but at temperatures between 100° and 125° the product consists almost entirely of the *metasulphite* described below, and known commercially as 'metabisulphite':

$$2Na.HCO_3 + 2SO_2 = Na_2S_2O_5 + 2CO_2 + H_2O.$$

Messrs. Boake & Co. (Pat. No. 4,262, 1888) prepare the commercial 'metasulphite' by passing sulphur dioxide through sodium carbonate or hydrate at a temperature varying from 43° to the boiling-point of the liquid. The solution, which has a sp. gr. of 1·4 to 1·45 when the reaction is finished, deposits the crystalline metasulphite on cooling.

The normal sulphite occurs in anhydrous, transparent, monoclinic, odourless, efflorescent crystals of cooling saline taste and of faintly alkaline reaction. The hydrated salt, which separates from cold solutions in transparent monoclinic crystals, contains 7 molecules of water. According to Muspratt (C. S. Mem. iii. 292; P. 50, 259), it has been obtained in large oblique prisms of the composition $Na_2SO_3.10H_2O$ by spontaneous evaporation of the solution over sulphuric acid. Schultz-Sellack (J. pr. [2] ii. 459) and De Forcrand (C. R. 98, 738) doubt the existence of the latter salt.

The hydrous salt becomes anhydrous when heated to 150°. According to Kremers the anhydrous salt dissolves in about 7·07 parts of water at 0°, 3·49 at 20°, and 2·02 at 40°.

The bisulphite crystallises in small shining anhydrous prisms possessing an acid reaction and a smell of sulphur dioxide. It may also be obtained with 4 or 9 molecules of water of crystallisation. It is largely used instead of the normal salt on account of the greater proportion of sulphur dioxide it contains.

When heated to dull redness, the sulphite is converted into a mixture of sulphate and sulphide: $4Na_2SO_3 = 3Na_2SO_4 + Na_2S$. When heated in dry sulphur dioxide gas at about 190°, the anhydrous sulphite is partially decomposed, a little sulphur being separated, with formation of some sulphate and thiosulphate (Divers, C. J. 1885, 208). The commercial salt usually contains thiosulphate, sulphate, and carbonate.

Among a large number of double sulphites of theoretical interest may be mentioned the sodium potassium salts (Hartog, *l.c.*, and Schwicker, B. 22, 1728) and the sodium ammonium salts (Schwicker, *l.c.*, Hartog, *l.c.*, and Röhrig, J. pr. 37, 217, and Touber, J. C. T. 1888, 444).

The metasulphite previously mentioned as being produced when sodium carbonate in hot solution is saturated with sulphur dioxide was first observed by Muspratt (C. S. Mem. iii. 292; P. 50, 259) in the form of monoclinic crystals. This salt was formerly known as the *anhydrosulphite*, but, according to Berthelot (C. R. 96, 142), should rather be considered as a metasulphite corresponding with the normal sulphite, as the metaphosphates correspond with the orthophosphates.

When heated to dull redness, it produces the sulphate, with separation of sulphur dioxide and sulphur:

$$2Na_2S_2O_5 = 2Na_2SO_4 + SO_2 + S.$$

The normal, bi-, and meta- sulphites are largely used (sometimes under the name 'leucogen') in various industries, principally as reducing agents and antiseptics and as sources of sulphur dioxide. The boiling solution has the power of readily dissolving the resin, gum, &c., contained in wood without in any way injuring the cellulose. Hence the bisulphite is used in preparing the 'sulphite pulp' now so largely made from wood for paper-making. It is also valuable to the calico-printer and colour maker as a reducing agent, as an 'antichlor' for removing the last traces of chlorine from the bleached pulp obtained in paper-making, and it is used in the composition of several colours for calico-printing. It is employed as an antiseptic for steeping grain, preserving food, &c., and medicinally as an antiseptic lotion and as an antizymotic for internal use. In photography it is largely employed in various developers for preventing oxidation of pyrogallol, and has been proposed by Abney (Phot. News, 1885, 370) as a substitute for thiosulphate in removing the unaltered silver salts in photographic printing.

Sodium sulphate, technically called 'sulphate,' or 'saltcake,' was first obtained by its discoverer, Glauber, as described by him in 1658, exactly in the same way as it is prepared now, by the decomposition of common salt by sulphuric acid. The crystallised salt, containing 10 molecules of water of hydration, is even now called 'Glauber's salts.' Both the anhydrous and the hydrated salts are found in many places in nature; the former, as a mineral, is called *thenardite*, the latter *mirabilite*. Large quantities of native sodium sulphate occur, especially in Spain, at Lodosa, in the Ebro valley, and elsewhere, and in the Western States of North America.

The double sulphate of sodium and calcium, called *glauberite*, also occurs naturally in large quantities and in many places.

Sodium sulphate is frequently obtained as a *by-product* of other manufactures, of which we mention only two.

Impure sodium sulphate is obtained in the (now almost obsolete) manufacture of hydrochloric acid in cast-iron cylinders from common salt and sulphuric acid; this product, called *cylinder-cake*, mostly contains from 7 to 10 p.c. of undecomposed sodium chloride. On the other hand, the *nitre-cake*, obtained in decomposing nitrate of soda by sulphuric acid, always contains a considerable proportion of hydrosodium sulphate, $NaHSO_4$.

A certain quantity of sodium sulphate, principally in the state of Glauber's salts, is made from the mother-liquors of salt-works, especially those producing salt from sea-water on the shores of the Mediterranean. Some more is yielded by working up the 'pan-scales,' essentially consisting of a mixture of sodium and calcium sulphates, and from the residues left on dissolving the crude carnallite ('Abraumsalz') at Stassfurt. The latter contains a large quantity of insoluble *kieserite*, $MgSO_4,H_2O$, which, on being exposed to the weather, or brought into contact with water for some time, gradually yields soluble magnesium sulphate, $MgSO_4,7H_2O$. The residues at the same time contain very much common salt, and, if necessary, more of the latter is added, so as to bring up the quantity to the proportion of 2 NaCl to 1 $MgSO_4$. When this mixture is dissolved in water and the solution is exposed to a natural or artificial cooling a few degrees below 0°, the following decomposition (noticed by Scheele as early as 1787) sets in:

$$MgSO_4 + 2NaCl = Na_2SO_4 + MgCl_2.$$

The sodium sulphate crystallises as Glauber's salts, the magnesium chloride remaining behind. Many thousands of tons of Glauber's salts are made at Stassfurt in this way.

The decomposition between *magnesium sulphate* and sodium chloride can also be brought about by heat; in the presence of water (*e.g.* when employing Epsom salts) hydrochloric acid is given off, and a mixture of sodium sulphate and magnesia remains behind, from which the former may be extracted by lixiviation. This process was tried in 1795 by Lord Dundonald, and in 1854 by Ramon de Luna.

Calcium sulphate has been experimented upon by many inventors in many ways, in order to transfer its sulphuric acid to the sodium of common salt; but this process seems to be useless. The same must be said of other sulphates tried for the same purpose. None of these processes has ever found any industrial application.

By *heating metallic sulphides with common salt in the presence of air*, sulphate of soda is produced in considerable quantities. This process has been known for at least a century in metallurgy, where it is employed for extracting silver and copper from their ores. In this case, of course, the metal is the product really aimed at, and the sodium sulphate is in actual practice run to waste in the shape of impure solutions. In 1842 Longmaid introduced a modification of this process, by which the sodium sulphate was obtained in a marketable form; but this was only practicable when employing ordinary iron pyrites, free from copper, and the sodium sulphate obtained in this way could not compete with that made in the ordinary way from common salt and sulphuric acid, as found out in the working of Longmaid's process in several places through a number of years. It is well known that a similar process is universally employed up to this day for the recovery of copper from cupreous pyrites; but here the sodium sulphate is lost, as mentioned above, all attempts to recover it having failed on account of expense.

Iron pyrites is, however, employed in a different manner for manufacturing nearly all the sodium sulphate found in trade—namely, either by first manufacturing sulphuric acid and employing this for decomposing common salt, or by the direct process of Hargreaves and Robinson, in which the pyrites-kiln gases are made to act upon common salt under such circumstances that sodium sulphate and hydrochloric acid are produced. We shall now describe these two processes.

The *decomposition of sodium chloride by sulphuric acid* is the process employed by Glauber, by Leblanc, and in the great majority of existing alkali-works. We shall omit mentioning the obsolete processes of performing this operation in glass retorts or iron cylinders, and merely describe the process as universally carried out at the present.

Excepting the case of mechanical saltcake furnaces (to be described further on), the decomposition of salt is now always carried on in two stages. Although the salt is at once mixed with enough sulphuric acid to convert it into normal sodium sulphate, this conversion is not attained at once, but at first only hydro-sodium sulphate is formed, half of the sodium chloride remaining behind:

$$(1)\quad 2NaCl + H_2SO_4 = HCl + NaHSO_4 + NaCl$$

Only on raising the temperature to a considerable extent a further reaction takes place, by which the decomposition is completed:

$$(2)\quad NaHSO_4 + NaCl = HCl + Na_2SO_4.$$

These two reactions are not, of course, quite sharply separated; in fact, during the first stage, which is carried out in the *decomposing-pan*, or *saltcake-pot*, from two-thirds to three-fourths of the total hydrochloric acid is given off at a comparatively low temperature, leaving only a third or a fourth for the second stage, the operation in the *roaster*, or *drying-furnace*. The decomposing-pan formerly used to be made of lead, but this has been mostly (in England universally) superseded by cast-iron, which admits of much more rapid work, and thus causes a great saving of labour, fuel, and interest.

The raw materials for this saltcake process are:

1. *Common salt*—that is, impure sodium chloride. In England almost exclusively 'pan-salt' is used, the porous condition and coarse grain of which is of great advantage in the process; it is also generally very pure, but contains varying quantities (up to 7 p.c.) of water. On the Continent rock salt is employed to a great extent; this must be coarsely crushed, not finely ground, and should be as free as possible from sulphate of lime. Cheshire rock salt contains too much ferric oxide to be directly employed in the saltcake process.

2. *Nitre cake*—that is, the residue from the manufacture of nitric acid, consisting of a

mixture of a normal and acid sodium sulphate. It must be tested for the percentage of the latter, and a quantity of common salt, just sufficient to decompose it into normal sulphate, must be added to the charge. It is decidedly advisable to grind the nitre-cake, preferably with the requisite quantity of common salt, and to add moderate quantities of this mixture to an ordinary charge of salt.

3. *Sulphuric acid.* This should be neither too weak nor too strong, preferably between 140° and 144°Tw.—that is, at the strength as it usually comes from the Glover tower. Stronger acid acts too rapidly, and yields badly mixed batches; weaker acid retards the operation, makes the condensation of the hydrochloric acid much more difficult, and greatly injures the pots.

The *saltcake-pots* are now always made in the shape of shallow cast-iron dishes, 9 to 11 feet in diameter, and 1 foot 9 inches to 2 feet 6 inches deep; the thickness of the metal varies from 5 to 7 inches in the centre, and from 2 to 3 inches at the sides. These 'pots' weigh from 5 to 6½ tons, and must be made of a special mixture, so as to combine resistance to chemical action with toughness and resistance to changes of temperature. Their edge is sometimes quite plain, sometimes provided with an ordinary horizontal flange; but, best of all, with an upstanding margin on a horizontal flange as shown in fig. 19 (*v.* p. 442). In the latter case they are arched over in such a way that the arch is sprung from the pan-edge itself, and that any leak occurring here cannot cause the escape of any hydrochloric acid into the fire-flues. The setting of the pan must be made very carefully, so that it receives an equal heating all over its bottom, and is never overheated in any one spot, which would cause it to crack very easily. This is best understood by reference to figs. 19 and 20.

On the Continent it is usual to dispense with a special fire for the pot, and to heat it by the waste fire of the roaster. It is true that the work cannot be done quite so rapidly in this way as with a separately-heated pot, but such an arrangement saves fuel, and is more conducive to a long life of the pot. It is particularly adapted to muffle-furnaces, and is sometimes used with those in England as well.

Near the decomposing-pan there must be a cistern for measuring the sulphuric acid to be run in for each charge. It is preferable that this acid should be moderately warm, and this can be attained by employing as gauge-vessel an iron pan lined with lead, and placing this over a hot flue.

The *calcining-furnace* (*roaster or drier*) may be of various patterns—either a reverberatory (*open*) furnace, or else a muffle-furnace (*close* or *blind* roaster). Open furnaces are mostly in use at the Tyneside works; they are easy to build and to keep in repair; they admit of a large quantity of work to be got out, and it is not possible with them for any acid gas to escape passing through the condensers. On the other hand, they require an expensive sort of fuel—viz. coke—in order not to stop up the condenser with soot, and, although it is quite as easy with them as with close furnaces to condense all the hydrochloric acid, so far as the requirements of the law are concerned, yet it is not possible to make that acid as concentrated as with close roasters. This possibility of obtaining a much larger quantity of strong hydrochloric acid is, indeed, the principal advantage of the close or blind furnaces, which are more prevalent in the other parts of the United Kingdom, and are exclusively employed on the Continent. This kind of furnace is much more difficult to build and to keep in repair than open furnaces. The quantity of work got out with them is decidedly less, and hence the cost of labour is more considerable; that of fuel is, however, less, since coal can be employed, and since the waste heat of the roaster is quite sufficient for heating the pot as well. The greatest drawback of blind furnaces used to be their liability to lose some of the acid gas by cracks in the bottom or roof of the muffle, and the majority of works were not always able to prevent this, even with the greatest care. Such acid, escaping into the fire-flues, necessarily missed passing through the acid condenser, and great damage to the surrounding vegetation was sometimes the consequence. This drawback is, however, avoided by employing 'plus-pressure furnaces,' in which the draught in the flue surrounding the muffle is less than within, so that in case of any leaks, in lieu of acid gases penetrating into the flues, on the contrary, a little of the fire-gas enters through the cracks into the muffle, without causing any appreciable damage to the work.

The higher pressure in the fire-flues outside the muffle can be brought about by various means—either by closing the ash-pit of the furnace and forcing in the air needed for the combustion of the fuel, by means of a fan-blast, or a Root's blower, or similar contrivance, or else by placing the fireplace much lower (say 4 feet) than in other furnaces, so that the heated fire-gases gain an ascensive force, corresponding to the height of the heated column, and thus enter the flues under the pressure desired. This system (invented by Deacon) not merely prevents the hydrogen chloride from passing away into the chimney, but it incidentally leads to a considerable saving of fuel—say, 30 p.c.—no doubt, owing to the fact that the supply of air, both below and above the fire, is more carefully regulated than in the old furnaces. Adding to this the saving effected by avoiding the frequent repairs always connected with stoppages that were needed to keep the old furnaces sufficiently tight to comply with the requirements of the Alkali Acts, the total saving is said to amount to 200*l*. per annum per furnace.

We shall now give illustrations of each kind of roaster. Figs. 19 and 20 show the usual Tyneside drying-furnace, with the pan attached to it, in sectional elevation and plan. *a* is the fireplace of the furnace, the area of which is comparatively small compared with that of the furnace-bed; *b* is the furnace-bed, with two working doors *f*; *c*, the outlet for the mixed fire-gas and acid gas; *d*, the decomposing pan, covered by an arch resting upon the pan flange; *e*, the gas-pipe; *h*, a balanced double cast-iron damper, which closes the passage *k* (fig. 20) (the 'shoving hole') between pan and furnace; *m*, the fire-grate of the pan, covered by the arch *n*, pierced by a number of holes; *o o*, a 'circular wall on which the pan is supported, equally pierced with holes, so that the flame escapes into the annular space outside, and thence into the main flue. It is evident how the setting of the pan aims at causing the flame to avoid striking the pan whilst it is hottest, and to distribute the heat as equally as possible.

The Saint-Gobain Company in 1891 still employed similar furnaces, in preference to mechanical furnaces, on account of the better yield of hydrochloric acid (Rapport du Jury, 1889, p. 70).

As an instance of a blind furnace we will show a 'plus-pressure furnace' on Deacon's system, in figs. 21 to 24. It is plainly shown here how the flame generated on a grate far below the top of the muffle is made to play, first on the top, then under the bottom, of the muffle, which is supported by a number of dwarf walls. The flame then travels on by an exit flue under the bottom of the pan, which is thus heated without any expenditure of special fuel.

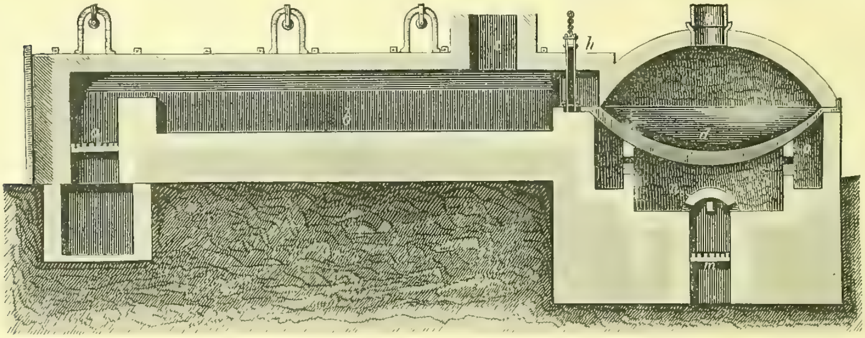

Fig. 19.

The work in saltcake making, as far as the pan is concerned, is almost entirely the same, whether the roaster be an open or a blind one. Only the size of the batches differs in both cases. With open roasters, which admit of finishing a batch once an hour, or even oftener, batches are made of 6 or 8, or at most 10, cwt. of salt. With close roasters, requiring upwards of two hours for each batch, they are in England made larger —15 to 16 cwt.; but on the Continent even then smaller batches are preferred. In any case, the pan, after removing the last batch, is carefully cleaned from crusts, which would burn fast and cause it to crack prematurely. It is then allowed to cool down to some extent, and the sulphuric acid, preferably heated up to some extent, is run in, whereupon the salt is charged, usually in the damp state, as it comes from the warehouse. Sometimes the salt is put in first and the vitriol run in afterwards. The quantity of the acid must, of course, be exactly regulated, and in measuring it in the gauge-vessel (comp. p. 441), not merely the volume and the hydrometric strength, but also the temperature of the acid must be carefully observed, since the specific gravity by itself is no index of the strength of acid, without taking into account the temperature. A table for reducing the specific gravities of sulphuric acid of various strengths to any other temperature between 0° and 100°C. is given in Lunge and Hurter's Alkalimakers' Handbook, 2nd edit. pp. 105 to 107.

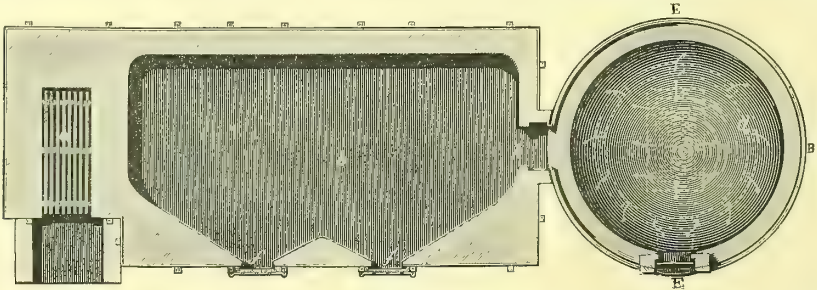

Fig. 20.

Theoretically, 100 parts of pure sodium chloride would require 83·82 parts of pure monohydrated sulphuric acid, or 106·28 parts of acid at 144°Tw., measured at 15°C. But common salt is never pure NaCl. This must be taken into account as well, by daily testing the salt at least for moisture, and allowing, say, 2 p.c. for other impurities. Thus, 100 parts of salt containing 95 p.c. of NaCl would take 79·63 parts of SO_4H_2 or 100·97 parts by weight of sulphuric acid of 144°Tw., measured at 15°C. This means $\frac{100{\cdot}97}{1{\cdot}72} = 58{\cdot}70$ litres of acid of 144°Tw. for each 100 kilos. of 95 p.c. salt, if the acid be measured at 15°C.; but, if the temperature were 100°C., the rates of the specific gravities (as per the table quoted above) is as 1·64 and 1·72, and hence the 58·70 litres will become = 61·56 litres, or, directly calculated, $\frac{100·97}{1·64}$ = 61·56 litres.

Practically a little more acid must be employed, partly because the mixture can never be theoretically perfect, partly because a little sulphuric acid or anhydride is volatilised, especially in the roaster. With open roasters this excess of vitriol required is about 5 p.c.; with close roasters, only 2 or 3 p.c. Whether the proportions employed have been correct or not must be decided in each particular case by testing of the saltcake, which ought not to contain above 0·5 p.c. undecomposed salt, or above 1 p.c. free acid (calculated as SO_3).

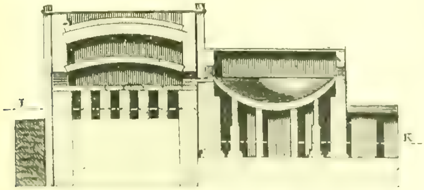

Fig. 21.

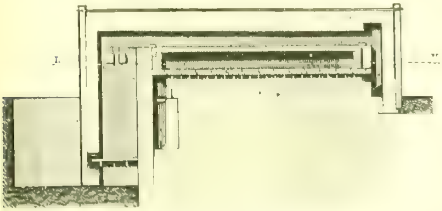

Fig. 22.

The first reaction between the ingredients in the saltcake pot is very violent, and there is a tendency of the mass to rise and to froth over, which is counteracted by throwing in a little tallow. The salt should be dissolved in the vitriol, which is easily done with common pansalt, but much less easily with rock salt, and is assisted by occasional stirring up, the handle of the rake passing through a hole in the charging door. The fire is then increased to drive off more hydrochloric acid, but not too much, lest the batch becomes too stiff; the work is regulated in such manner that the batch is ready to be 'cast' or 'shoved' into the roaster, just when the last charge has been drawn from the latter. For this purpose the damper *h* (fig. 19) is raised. The work in the roaster must be carried on in such manner that the batch is thoroughly turned over and mixed. The cooler portions are gradually brought forward towards the firebridge, where the temperature is highest and all the lumps are crushed, because otherwise undecomposed salt would remain in their central portion.

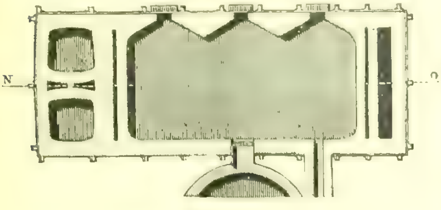

Fig. 23.

The temperature within the furnace should ultimately be a bright-red heat, and no more vapours should be seen rising from the mass. Still, it usually happens that, on drawing the batch out of the furnace, copious vapours are given off (those of sulphuric anhydride being less pungent than those of hydrogen chloride), and, to avoid any nuisance, the mass is frequently first drawn into a cave, where it cools down and is then removed without causing a nuisance.

The yield of saltcake is very nearly that calculated by theory from the dry salt. It may be taken as 116 to 120 parts upon 100 of dry salt. Calculated upon the sulphur burnt in the pyrites kilns, it varies from 405 to 430 parts to 100 of sulphur actually burnt, open furnaces yielding rather less than close ones (owing to the volatilisation of some SO_3).

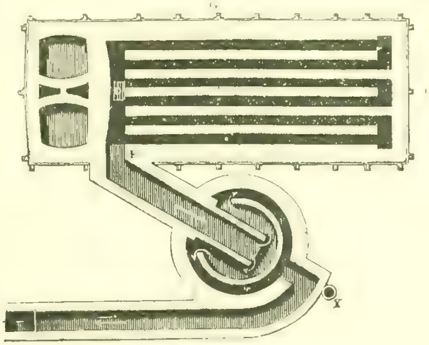

Fig. 24.

The consumption of coals varies from 30 to 50 parts to 100 of saltcake; it is higher with close roasters than with open ones, but the difference is less where the pans are heated by the waste fire of the muffle-furnace. Mactear (S. C. I. 1811, 31) states it per ton of saltcake, with Newcastle open roasters = 4·29 cwt. coke and 2·70 coals (for the pan); with Glasgow close roasters = 10 cwt. of coals; with his mechanical furnaces = 4·5 cwt. coke or an equivalent of gaseous fuel. The 'Wilson' gas-producer has been found very efficient with mechanical furnaces.

Mechanical saltcake furnaces have been constructed by many inventors, chiefly with the view of dispensing with the great risk of breaking pans through the carelessness or inexperience of workmen, and, of course, to economise labour and coals. We mention among such furnaces those of Jones and Walsh (1875; improved in 1887; *cf.* C. N. 35, 51); Black and Hill (1877); Cammack and Walker (1876); Black and Larkin (1884). Some of these have not answered in the long run, and we shall confine ourselves to a description of one of the most successful of mechanical salt-cake furnaces, that of Mactear (1879, accurately described and discussed S. C. I. Proc. of first

General Meeting, 1881, p. 29 *et seq.*), as shown in fig. 25. It consists of a revolving circular bed, covered by a fixed arch, the fire passing between them and the access of air being prevented by a 'lute' filled with saltcake. In the centre there is a kind of pot into which both salt and acid are continuously fed, and in which they are mixed. The pasty mass overflows into the outer beds, and is both continually stirred and gradually carried to the outer circumference by means of a number of stirrers, which are protected against the action of the fire and the acid gases by being placed between the gas-flues. The finished saltcake, arriving at the outer edge, falls into the delivery trough running all round the furnace, and at the same time forming the 'lute.' The acid vapours and products of combustion pass away together in two flues, arranged at each side of the row of stirrers. The bed of the furnace is lined with fire-brick, boiled in tar and set in a special cement, which becomes even harder when subjected to the action of the heat and sulphate.

A great point in the Mactear furnace is the continuous decomposition of salt. Thus a continuous and even stream of hydrogen chloride is evolved, and, although this is mixed with all the fire-gases, the condensation of the acid is comparatively easy through the extreme regularity of the process. The flow of water need not be altered for days, and the hydrochloric acid, it is asserted, can be condensed at a strength of 28° or 30°Tw., no weak acid being produced (compare, however, the French statements below). It is claimed that the condensing-plant required is decidedly less that that found necessary with close furnaces. Mr. Mactear states the condensing-space required for his mechanical furnace = 120 cubic feet per ton of saltcake. Mr. Carey (*l.c.* p. 39), for Lancashire close roasters = 150 cubic feet (in 1881). Mr. Mactear, for Tyneside open roasters = 400 cubic feet. Each furnace can finish one ton per hour, or 144 tons per week of six days, with only one man to do the work, and an engineman for each two furnaces. Rock salt can be employed in them, and the quality of the sulphate is excellent.

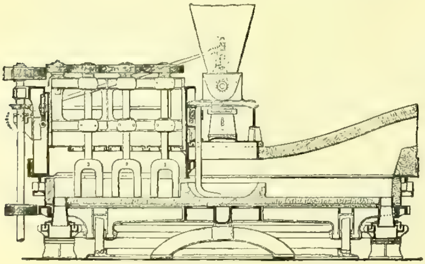

FIG. 25.

The Mactear furnace was first fired with coke; then 'Wilson producers' were attached to it (compare above); but in France these have had to be given up again for coke, so that the hoped-for economy in firing has not been realised. The difficulty of obtaining strong hydrochloric acid has also been found much greater than had been anticipated. Although the condensing-plant at St. Gobain has been greatly enlarged for this purpose, and the gases are cooled down to 40° or 50°C. before entering the condensers, the acid cannot be made stronger than 28°Tw., and in England it is often only made = 22°Tw. The quality of the sulphate, however, is very good (Official French Exhibition Report, 1891, p. 72).

The Black and Larkin furnace, which is combined with an ordinary pan, is a peculiarly-constructed muffle, heated from without by a number of small fires, both above and below, practically on the 'plus-pressure' system, with a very efficient mechanical stirring apparatus, thus admitting all the work to be done with closed doors, and avoiding 'low-level escapes.' Naturally the condensation of the hydrochloric acid is quite as easy in this case as with ordinary close roasters. One such furnace decomposes from 72 to 80 tons of salt per week, and furnishes enough hydrochloric acid to make 46 cwts. of bleaching powder from 20 cwts. of salt. These furnaces have been found very successful, and are still at work in the place where they were originally introduced. Another mechanical furnace, composed of two revolving cylinders, is that of A. Walker (Eng. Pat. 9,760, 1887).

The direct process of manufacturing sulphate of soda from common salt, sulphurous acid, and air, without the intervention of sulphuric acid, has been the subject of many efforts, commencing with Gossage's, in 1850. None of these had any practical success till Hargreaves and Robinson (beginning from 1870) introduced a number of improvements which have made that process practicable and entirely successful. We shall here describe it in its improved shape.

The process consists in conducting the gases from pyrites kilns of something like the usual principle, mixed with a suitable quantity of steam, through a series of large cast-iron cylinders, charged with common salt, in such manner that the fresh gas meets with the salt which has been the longest time exposed to the treatment, whilst the nearly-exhausted gas is brought into contact with fresh common salt. In this wise it is brought about that, on the one hand, the salt is completely converted into sulphate, and, on the other hand, the pyrites kiln gases are quite as fully utilised as they would have been by passing them into vitriol-chambers, hydrogen chloride taking the place of sulphur dioxide. The reaction:

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl,$$

takes place at a temperature of about 500° to 550°C., and this must be maintained against the radiation into the surrounding space by external heating; but as the above reaction itself produces heat, the amount of fuel required is not exorbitant—at least, if every care is taken against undue loss of heat during the process. This is all the more necessary, as the process is a slow one: it takes from two to three weeks before the salt, charged into one of the cylinders, can be taken out in the shape of finished saltcake.

The first step is bringing the salt into such shape that the gases can readily pass through it and yet reach all parts of it to the very core. After many attempts, the following plan was found to be entirely successful: The salt is crushed and moistened by exhaust steam. It then falls from a hopper upon an endless chain of plates, each of them 12 inches broad and 5 feet across, of a total length of 100 feet, or more, rising up in a sloping oven and returning underneath the same. On falling upon that travelling-platform the salt is mechanically beaten down into a layer of 1 to 1½ inch thickness, which is at once cut, by means of mechanically-moved knives, into cakes about 3½ inches square. These now enter into the oven, which is heated by the waste-fire of the cylinders, and pass through it at such a rate that they arrive perfectly dry at the upper end. As the chain turns downwards the dry cakes detach themselves and fall down upon a grating. They are now dense enough to retain their shape in the cylinders, and yet porous enough to be entirely penetrated by the gases, their regularity of shape securing regularity of draught in the process.

The decomposition of the salt takes place in a series of cylinders, from 8 to 20 in number, about 15 feet in diameter, and 12 feet high, and holding 40 tons of saltcake, or even more. They are surrounded by small vertical flues connected with a fireplace below, and their tops are protected against cooling by a thick layer of ashes. Inside there is a movable grate, on which the salt rests. A number of manholes in the top serves for charging; a large door above the bottom for discharging. A set of large cast-iron pipes serves for admitting the burner-gas at once into any of those cylinders and for passing it through the whole series, the gas always entering at the top and going away at the bottom. The connections between the main gaspipe and any one cylinder and those between the single cylinders are opened or closed by a very simple arrangement—viz. by dividing the connecting elbow pipes or 'siphons' in two halves, and either shutting the connection by inserting an iron plate or else leaving it open, always luting the joint by a mixture of mortar and salt. From the last cylinder of the series the gases pass, through an opening in the bottom of the drawing doorway, into a flue, whence they are withdrawn by a Root's blower, and sent into the hydrochloric acid condenser.

The diagrams (figs. 26 and 27) show such a set of 8 cylinders, seen from the top and in section.

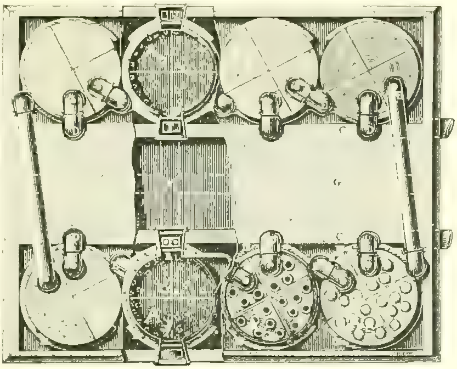

FIG. 26.

A_1 to A_8 are the cylinders, B the discharging doors, C C the iron pipes for burner-gas with their connecting siphons D and circulating siphons E; F is the outlet opening, G the gas-flue for the exit gas; J is an opening in the top by which cold air can be admitted, in case the cylinders get too hot.

The pyrites burners employed are specially constructed with a view to avoiding radiation and sending the gas as hot as possible into the cylinders. The necessary steam is superheated by the waste heat of the gases, and is usually introduced in the upper part of the burners.

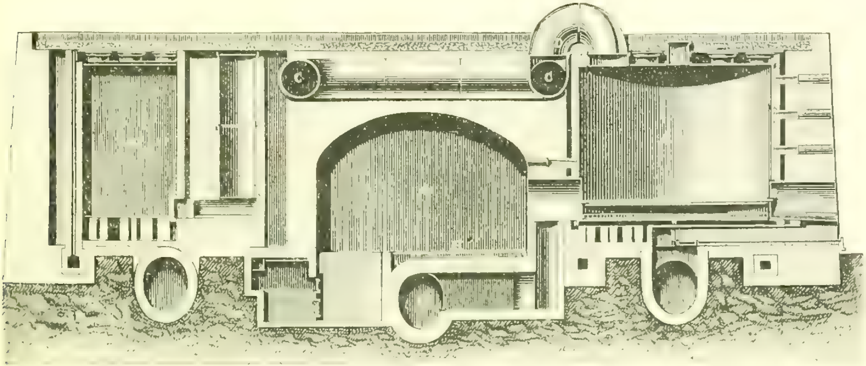

FIG. 27.

The movement of the gases through the whole system is produced by means of a Root's blower, placed between the cylinders and the acid condensers. By keeping the blower so hot that no liquid acid can be condensed in it, it is protected against any action of the acid; but the ends of the shaft, passing through the blower, must, on the outside, run in water-cooled bearings. The exhaust steam of the engine is utilised for the steam required for mixing with the burner-gas.

The amount of fuel required in a special case was as follows (calculated upon 20 cwts. of saltcake):

For heating cylinders . .	4 cwts.
For preparing salt . .	3 ,,
For steam	0·75 cwt.
	7·75 cwts.

In other cases nearly 10 cwts. of fuel has been required, but in any case no more fuel is needed than in the ordinary process of making sulphuric acid and employing this for decomposing the salt. In the largest and best-designed plants the fires for heating the cylinders from without are not needed at all, the heat of the reaction sufficing to make up for the loss by radiation.

The amount of sulphurous acid lost with the exit gas is stated not to exceed 2 p.c. The condensation of the hydrochloric acid, although it is mixed with so much inert gas, is greatly facilitated by the absolutely regular and continuous evolution of the hydrogen chloride, but care must be taken to thoroughly cool the gas before it enters the condenser.

The quantity of the saltcake obtained by the Hargreaves' process entirely depends upon the care taken in conducting it, especially in keeping the temperature neither too high nor too low. In the latter case the action is imperfect; in the former, the salt fluxes, and the interior parts are not converted into sulphate, which is indicated by their reddish colour (caused by the decomposition of ferric sulphate into ferric oxide). With proper care, the average strength should be quite as good as with the ordinary process—say 97 p.c. —and the comparative freedom of the Hargreaves' sulphate from iron is a great advantage for its use in glass-making.

A new patent of J. Hargreaves, T. Robinson, and J. Hargreaves (Eng. Pat. 5,682, 1886) contains a number of improvements on the old plan.

The advantages of the Hargreaves' process are: a very large saving of space in comparison with vitriol chambers and decomposing pans; emancipation from the risk of breaking pans; comparative freedom from nuisance; saving of all nitrate of soda; steady evolution, and hence easy condensation, of hydrochloric acid, in spite of its dilution with inert gases; production of sulphate almost free from iron.

The drawbacks are: the extreme care required for keeping everything in order, since a mistake in any one cylinder at once spoils 40 tons of saltcake; and the very high cost of plant, which does not, like chamber lead, retain a great portion of its value when worn out. It is also very difficult to make strong hydrochloric acid; usually it gets up to no more than 25° or 27°Tw.; but at Hautmont, by greatly increasing the number of bonbonnes, they get up to 32°Tw. These drawbacks, connected with the fact that about the time when the Hargreaves' process had been fully worked out, a great depression in the alkali trade set in, which prevented capitalists from spending large sums of money in erecting new alkali works, followed by the demonstration of the economical superiority of the ammonia process over the Leblanc process of soda-making, has caused the Hargreaves' process to be much less introduced into practice than would undoubtedly have been the case under other circumstances. It is, however, in current work at several English and two French alkali works.

Saltcake free from iron (or nearly so) is required especially for plate-glass, window-glass, and so forth. The Hargreaves sulphate is frequently pure enough for this purpose. On the Continent it is usually made by employing decomposing pans made of lead, which are certainly much more difficult to manage than the cast-iron pots otherwise used. The batch must be taken out much thinner, and the firing must be much more careful than with cast-iron pots. Sometimes refined sulphate of soda so made by dissolving ordinary saltcake in a similar way to soda (p. 477), adding a little lime and bleaching powder in order to precipitate the iron, settling, boiling down the clear liquor and drying in a furnace, just like refining alkali (p. 475). Schmaltz and Löwig (Germ. Pat. 23,378) describe a special process for manufacturing sulphate free from iron, based on the application of kieserite.

Glauber's salt is crystallised sodium sulphate $Na_2SO_4,10H_2O$. It is manufactured for a few purposes, principally for medicinal use and for freezing mixtures. A considerable quantity is obtained from the residuals of the Stassfurt salts, and from the mother-liquor in the manufacture of sea-salt. Some more is made by dissolving ordinary good saltcake, adding a very little lime and bleaching powder to precipitate any iron present, settling and running into coolers for crystallisation. It is required in two very different states—viz. in very small or in large crystals. The small acicular crystals ('Epsom salt fashion') are obtained by making the solution as strong as possible at a temperature of 34°C., settling, running into shallow coolers, and stirring the solution until it has cooled down. The larger crystals ('soda fashion') are made by dissolving the sulphate at 50°C., till the sp.gr. is =1·257 (at 40°C.), settling for an hour, and running into deep coolers (2 to 5 feet depth), where the liquor is kept quite undisturbed. In order to facilitate the formation of large crystals, wooden staves or pieces of twine, weighted with a little lead, are hung in the vats. The cooling lasts from 5 to 20 days, according to the size of the vats and the season, the crystals are large (an inch and more thick), hard and shining, and they must be dried at a temperature not exceeding 30°, to prevent efflorescing.

The inverted process, that of dehydrating Glauber's salt, when obtained as a cheap by-product, is somewhat troublesome, owing to the melting of the salt in its water of crystallisation and the formation of hard crusts. Where at the same time common salt, or magnesium sulphate, or a mixture of both, are available at very small cost (as in the working up of mother-liquors from sea-salt), these salts may be melted with Glauber's salt at a temperature of 40° or 50°C., when anhydrous sodium sulphate is precipitated, and is separated from the solid substances by centrifugal force (Péchiney, 1878).

In most cases, *e.g.* at Stassfurt, the process just described is not practicable, and it is also said to yield sulphate containing much chloride. It is here usual to heat a saturated solution of Glauber's salt in an iron pan, covered by an arch and heated from the top by the waste fire of a reverberatory furnace which returns below the bottom of the pan; anhydrous or monohydrated sodium sulphate separates out on concentration, and is removed by fishing it out with a perforated ladle, whereupon it is calcined on the hearth of the just mentioned furnace. This process might evidently be carried on very well in a Thelen's pan.

Testing of saltcake.—In current work saltcake is only tested for free acid and undecomposed salt. The former is found by titrating with standard soda solution, using methyl-orange as indicator, and is generally calculated as SO_3. The latter is found by adding to a fresh sample exactly as much soda as had been required in the first test, so that the acid is completely neutralised, then a little potassium chromate as indicator, and titrating with decinormal silver solution. Sometimes it is required to guarantee a maximum percentage of iron; this is found by reducing with zinc and titrating with potassium permanganate. For estimation of lime, alumina, &c., and direct estimation of Na_2SO_4 comp. Lunge and Hurter's Alkalimakers' Handbook, p. 117.

Statistics.—The quantity of saltcake made in the United Kingdom can be inferred from the following statistics[1]:—

Salt decomposed by the Leblanc process.

In 1852	137,547 tons	In 1881	620,064 tons
,, 1860	250,000 ,,	,, 1882	598,833 ,,
,, 1871	352,350 ,,	,, 1883	602,921 ,,
,, 1876	538,600 ,,	,, 1884	578,874 ,,
,, 1877	552,570 ,,	,, 1885	591,478 ,,
,, 1878	535,154 ,,	,, 1886	584,323 ,,
,, 1879	575,447 ,,	,, 1887	577,381 ,,
,, 1880	648,587 ,,	,, 1888	590,312 ,,

In France the following quantities of salt have been decomposed:—

In 1878	117,015 tons	In 1884	125,695 tons
,, 1880	125,317 ,,	,, 1886	120,001 ,,
,, 1882	123,911 ,,	,, 1888	107,020 ,,

In Germany:—

In 1886	225,067 tons	In 1888	207,417 tons
,, 1887	220,810 ,,	,, 1889	251,450 ,,

Most of the saltcake produced is consumed for the manufacture of soda ash by the Leblanc process; the remainder, about 80,000 to 90,000 tons per annum, is chiefly consumed by glass-makers. G. L.

Sodium thiosulphate (hyposulphite)

$Na_2S_2O_3 + 5H_2O$.

This compound was first prepared in 1799 by Chaussier. Small quantities of the salt may be made by taking about 1 pound of pure, well-dried sodium carbonate, mixing with it about one-third its weight of flowers of sulphur, and then heating the mixture in a porcelain basin to the melting-point of sulphur for some time, stirring well all the while, so as to bring every part in contact with the air. Oxygen is absorbed by the sodium sulphide formed, and is converted, with feeble incandescence, into sodium thiosulphate. When cold, the mass is dissolved in water, boiled with sulphur for some time, and the liquid concentrated by evaporation to the crystallising-point. A very pure product may be thus obtained. The earthy thiosulphates are obtained by exposing their sulphides to the oxidising action of the air; and upon this principle depends Losh's process, which is as follows: The tank waste produced in alkali works is exposed to the air for a week or more, being turned over from time to time, to bring every portion in contact with air. The mass is then lixiviated with water, and, the thiosulphates of sodium and calcium being now in solution, on adding sodium carbonate solution, the calcium is precipitated as carbonate, while the whole of the thiosulphuric acid is converted into the sodium salt. The solution is drawn off from the insoluble precipitate, concentrated by evaporation, and the crystals of sodium thiosulphate obtained are purified by recrystallisation. A modification of this process, by Kopp, is as follows: The tank waste is mixed with 10 to 15 p.c. of sulphur and 12 to 15 times its weight of water, and is then boiled for an hour. The solution of polysulphide obtained is put into a closed apparatus, in which it can be agitated, and is treated with sulphurous acid. The solution now contains calcium thiosulphate, and is converted into the sodium salt by addition of sodium sulphate. The solution of sodium thiosulphate is drawn off from the precipitate of calcium sulphate, and is concentrated and crystallised as before.

The preparation of sodium thiosulphate has been carried out as follows: Strontium sulphide—obtained by reducing strontium sulphate by means of powdered coal—is, while still hot, mixed with water to form a thin paste. The mass is boiled with sufficient caustic alkali to convert the sulphite into sulphate. Strontium hydrate crystallises out on cooling, and the mother-liquor consists of solution of sodium sulphide. On treating this liquor with sulphur dioxide, sodium thiosulphate is formed, and free sulphur deposited (S. C. I. 3, 30).

Sodium thiosulphate may also be prepared from the spent lime of the purifiers of gas works, which contains the calcium salt of thiosulphuric acid as well as calcium sulphide.

The salt forms large transparent prisms, belonging to the monoclinic system. Its solution is neutral to test paper; it is without smell, has a cooling taste, and does not change on exposure to air. The crystals melt in their water of crystallisation at 45°, all the water being expelled at 215°; and at 220° they decompose, with separation of sulphur (Pape). The salt has a sp.gr. of 1·672, is extremely soluble in water, but does not dissolve in alcohol. The aqueous solution decomposes on keeping, depositing sulphur, and is partially converted into sulphate. When treated with sodium amalgam, it gives sodium sulphide and sulphite:

$$Na_2S_2O_3 + Na_2 = Na_2SO_3 + Na_2S.$$

Uses.—Sodium thiosulphite is used by the photographer for dissolving salts of silver. The photographic paper and plate, after printing and exposure in the camera respectively, are 'fixed' by a solution of this salt, which dissolves out the salts of silver which have been left unchanged during the exposure. The paper-maker uses it as an 'antichlor,' to remove the last traces of chlorine employed in bleaching the pulp. In calico-printing it is used as a mordant; aluminium chloride is treated with sodium thiosulphate, by which means aluminium thiosulphate is obtained. This is thickened as usual and printed on the fabric, and, on exposing to a temperature of 100°, alumina is deposited on the cloth and dyes with madder, in the same way as that from the acetate. It is used in fixing aniline greens upon the fibre, and is known in the

[1] Extracted partly from S. C. I. 1886, 412.

trade as 'green mordant.' In conjunction with salts of copper it has been employed in the production of the so-called 'argentine effects,' which depends upon the deposition of a thin film of copper sulphide on the fibre.

Sodium thiosulphate is employed in the separation of iron and aluminium. A solution containing these two metals is treated in the cold with sodium thiosulphate; this gives rise to the aluminium thiosulphate, and, when boiled, the latter is decomposed, with evolution of sulphur dioxide and deposition of sulphur and alumina. By throwing the whole on a filter, the iron, still in solution, passes through.

The property which this salt possesses of fusing at a low temperature in its own water of crystallisation and readily solidifying again on cooling, has been utilised by Fleck in sealing glass tubes containing explosives to be used under water in torpedoes.

Sodium thiosulphate is used in medicine in cases of sarcinous vomiting, to check fermentation, and as an external application in parasitic skin diseases. It is not irritating like sulphurous acid.

Sodium thiosulphate is used in metallurgy to separate silver from ores containing also copper, lead, iron, zinc, nickel, &c. The ore is first roasted with common salt, and the chloride of silver is dissolved out by a solution of sodium thiosulphate (*v.* SILVER).

It is also used in estimating the copper in gun-metal, and is well adapted for determining the copper in commercial varieties of the metal, in bronze, &c., where lead or iron is not present in large quantity. The process depends upon the reaction between iodine and thiosulphuric acid, the reaction being complete when the iodide of starch formed is bleached. It is also employed in the wet assay of copper. The ore is first decomposed with sulphuric and nitric acids; the filtered liquid, after boiling, is treated with sodium thiosulphate, which precipitates disulphide of copper, liberates sulphur dioxide, and throws down sulphur. After drying the precipitate and burning off excess of sulphur, the remainder is weighed as copper sulphide, 100 parts of the sulphide giving 79·85 parts of copper.

Sodium thiosulphate has been proposed as a substitute for sulphuretted hydrogen in qualitative analysis. The process consists in precipitating the first group with hydrochloric acid as usual, then precipitating lead, barium, strontium and calcium in part as sulphates, boiling the filtered solution with sodium thiosulphate (1 part of the crystallised salt to 5 parts of water). This precipitates copper, mercury, bismuth, arsenic, antimony, and tin salts. The necessary conditions are that (1) the solution to be examined must not contain much free acid nor any nitric acid; (2) the thiosulphate must be added in small quantities at a time, and not in excess (G. Vortmann, M. 7, 418).

Sodium nitrate (*cubic nitre*; *Chili saltpetre*) $NaNO_3$. This important salt occurs as *nitratine* in the natural and artificial accumulations of potassium nitrate, and in other deposits where it has been produced similarly to that salt (*v.* POTASSIUM NITRATE).

The natural occurrence of the sodium nitrate, as distinguished from the potassium salt, does not appear to have been fully recognised until the present century, for it is stated in Rees' Encyclopædia, 1819 (art. NITRATE OF SODA), that it had not been found up to that time in a native state, although its manurial value had already been recognised by Lord Dundonald.

Sodium nitrate occurs in almost inexhaustible quantities, and practically free from the potassium salt, in the province of Tarapaca in South America, and this, with the exception of certain deposits on the coast of Bolivia, constitutes the only source from which the salt is extracted on the large scale.

The nitrate deposits do not form beds of any definite character, but represent the outcrop of a bed of salt which appears to have been left at the bottom and sides of ancient tidal lagoons by the upheaval of the coast. Although the district is now extremely arid and only receives rain at intervals of three years or more, there is abundant evidence of former fertility in the large quantities of buried trees and other vegetation which are found in the vicinity, together with guano and fish remains, sea-shells, and other substances of marine origin.

The nitrate may be regarded as the product of the decomposition of this organic matter in presence of carbonate of lime and the salt left by the evaporation of the sea-water. This view is borne out by the composition of the deposit, especially by the presence of sodium iodide and iodate and of salts of magnesium and calcium. The nitrification appears to have occurred only at the outcrop of the salt, for the nitrate diminishes in quantity towards the middle, and is practically absent at the centre of the deposit.

The main nitrate belt of Tarapaca has a width of about $2\frac{1}{2}$ miles, and is included between latitudes 27° S. and 19° S. for a total length of about 260 miles. It stretches along the eastern slope of the coast range of the mountains which extend from the northern limit of Peru to the Straits of Magellan, and which have an average height of about 2,000 feet.

The deposit occurs some 500 or 600 feet higher than the valley of Tamaragal, and diminishes in richness as the valley is approached, the nitrate disappearing altogether at the bottom. The average distance from the sea coast is about 14 miles, but some of the deposits are as far distant as 90 miles.

The 'caliche,' as the crude nitrate is called, is never found at any great depth. It is usually covered to a depth of 6 or 10 feet by a crust or 'costra,' consisting of a conglomerate of porphyry, felspar, magnesia, sodium chloride, &c., cemented together by gypsum, and covered by a layer of fine loose sand to a depth of 8 or 10 inches. The caliche proper forms a rock-like mass from 4 to 6 feet deep, and varies in colour from almost pure white, through shades of yellow, orange, brown, bluish grey, &c. The lower part of the caliche (known as 'congelo') contains but little nitrate, and abounds in the chlorides of sodium and magnesium, and in sulphates. It lies upon a pale, yellowish-brown, loose clay free from nitrate, and overlying the primitive rock.

Various qualities of caliche are worked, varying from 40 p.c. to 50 p.c. in the best quality, to 30 p.c. to 40 p.c. in the second, and 17 p.c. to 30 p.c. in the inferior kinds.

The Tarapaca deposits were worked as early as 1813 by the Spaniards, who exported 23,732 quintals (of 100 pounds) in that year; but the industry was but little developed until 1852, when small refining works were established by Smith and Sandes. The output then increased to over 60,000 tons in 1860, and since that time the industry has progressed continuously, until in 1888 about 764,000 tons, and during the ten years ending December 1888 over 4,574,000 tons, were exported.

The method of separating the nitrate from the caliche consists merely of a careful system of lixiviation. At the Officina of Ramirez (Tarapaca) the caliche is crushed roughly into 2-inch lumps, and is boiled in long tanks heated by steam coils. When the liquid acquires a specific gravity of 110°Tw. it is run off into crystallising tanks, the residual 'ripios' being washed with a further quantity of water, which is used for treating the next batch of caliche. The refuse contains only about 3 p.c. of nitrate. The crystallised nitrate is drained, dried by the heat of the sun, and at once packed in bags for exportation. The mother-liquors ('aqua vieja') are concentrated and treated for the separation of the iodine, which amounts to about 50 grms. for 100 kilos. of caliche. The importance of this by-product is shown by the fact that in the ten years ending December 1888 no less than 1,588,000 kilos. of iodine was exported from the various South American ports (*v.* Iodine).

The following analyses show the composition of caliche and Chili saltpetre: (1) Shows the composition of one of the largely-worked deposits (Forbes, Phil. Mag. 32 (1866), 135); (2) shows the composition of that worked at the Officina Ramirez (Harvey, Proc. Inst. C.E. 82 (1885), 337); and (3) and (4) are analyses of the better and inferior qualities of nitrate sold for agricultural purposes (Macadam, S. C. I. 1888, 96):—

—	(1)	(2)	(3)	(4)
Sodium nitrate .	21·01	51	98·44	94·23
Sodium chloride	55·27	26	0·14	4·54
Sodium sulphate	4·74	6	—	0·13
Calcium chloride	0·33	—	—	—
Potassium iodide	0·87	—	—	—
Aluminium sulphate. . . .	9·81	—	—	—
Magnesium sulphate. . . .	5·93	3	—	—
Insoluble matter	2·04	14	0·04	0·15
Moisture	—	—	1·38	0·95
	100·00	100	100·00	100·00

Further information on these deposits will be found in the works of Sturzer (Nitrate of Soda, 1887; edited by Wagner) and Billinghurst (Estudio sobre la Geografia de Tarapaca, and Chem. Zeit. 11, 752), and in the various Consular reports to the British and United States Governments.

Sodium nitrate is obtained when sodium carbonate or hydrate is dissolved in nitric acid, or when common salt is boiled with that acid. On the large scale, however, it is always obtained from the natural product by repeated crystallisation. The last traces of chloride are best removed by adding a small quantity of nitric acid to the boiling saturated solution of the salt, and recrystallising.

The crude nitrate is a pale-grey or yellowish-white salt, usually containing 94 to 98 p.c. of nitrate, from 0·1 to over 4 p.c. of sodium chloride, and from 0·6 to over 2 p.c. of moisture.

The pure salt forms transparent, colourless, anhydrous rhombohedra, whose angles closely approximate to right angles, whence its name 'cubic nitre.' It fuses at 316° (Carnelley, C. J. 33, 276); at higher temperatures—lower than that at which potassium nitrate decomposes—it evolves oxygen with production of the nitrite, and on further heating it gives off nitrogen and nitrous fumes, leaving a residue of sodium monoxide and peroxide. The salt as usually obtained is hygroscopic; but, according to Gentele (D. P. J. 118, 203), this is due to the presence of the nitrates and chlorides of calcium and magnesium, and is not observable in the pure salt.

According to Ditte (C. R. 80, 1164) 100 parts of water dissolve the following proportions of the salt:—

At 0°	66·69	At 18°	83·62
2°	70·97	21°	85·73
4°	71·04	26°	90·33
8°	75·65	29°	92·93
10°	76·31	36°	99·39
13°	79·00	51°	113·63
15°	80·60	68°	125·07

When saturated at 0° the solution may be cooled to −15·7° without crystallisation; but at that temperature the salt separates out in fine laminated plates built up of fine needles lying side by side. A hydrate of the composition $NaNO_3.7H_2O$ appears to exist (Ditte, *l.c.*).

Sodium nitrate dissolves in glycerin, but is almost insoluble in absolute alcohol; 100 parts of alcohol of 16·4 p.c. dissolve 21·25 parts of the salt (Pohl, Sitz. B. 6, 600).

It is used for many of the purposes for which the potassium salt is employed; but its hygroscopic nature renders it inapplicable for the manufacture of gunpowder or fireworks, &c. For the making of nitric acid, for supplying that acid in the sulphuric acid manufacture, and as a manure, it has, however, entirely replaced potassium nitrate. It is also the principal source of that salt, which is obtained from it by double decomposition with the potassium chloride of Stassfurt.

Sodium hypophosphite NaH_2PO_2 may be prepared by boiling aqueous or alcoholic soda with phosphorus until evolution of phosphoretted hydrogen ceases

$(6NaHO + 2P_4 + 6H_2O = 6NaH_2PO_2 + 2PH_3)$.

The solution is poured off, treated with sodium bicarbonate to convert any unchanged soda into carbonate, and is evaporated and treated with absolute alcohol, which dissolves the hypophosphite only. The salt crystallises out on cooling.

For pharmaceutical purposes it is usually prepared by double decomposition between solutions of sodium carbonate and calcium or barium hypophosphite (*v.* Phosphorus oxides and Oxy-acids). The filtered solution is evaporated on the water-bath with frequent stirring as the mass becomes syrupy, in order to obtain a granular salt. To obtain the salt free from phosphite, Boymond (Ph. [3] 10, 407) treats 25 grms. of the commercial salt with 1 grm. of barium hypophosphite in solution, and dilutes to 50 c.c., adding 200 c.c. of strong alcohol after a time. The liquid is settled and filtered from the precipitated barium phosphite and hypophosphite, and the last traces of barium having been removed by careful addition of sodium nitrate, is filtered and mixed with 500 c.c. of strong alcohol and a sufficiency of ether. The pure hypophosphite which separates is dried in a current of air.

Sodium hypophosphite crystallises in small, pearly, rectangular, very deliquescent plates containing one molecule of water of crystallisation. It dissolves at 15° in 1 part of water, and at 100° in 0·12 parts. It is also soluble in alcohol. The aqueous solution absorbs oxygen from the air with formation of phosphite (Wurtz, A. Ch. [3] 7, 37).

When heated to 200° the crystals become anhydrous, and on further heating become converted into metaphosphate and pyrophosphate, with evolution of hydrogen and spontaneously inflammable phosphoretted hydrogen:

$$5NaH_2PO_2 = Na_4P_2O_7 + NaPO_3 + 2PH_3 + 2H_2.$$

It explodes when triturated or heated with an oxidising agent, and has been known to explode during evaporation on the water-bath (Am. J. Pharm. 1860, 87).

Sodium hypophosphite is a powerful reducing agent, and precipitates gold and silver from solution. It is used medicinally.

Sodium phosphates. A considerable number of these salts belonging to the three classes ortho-, pyro-, and meta- phosphates, together with a large series of double salts, are known. The three classes of salts may be distinguished by their behaviour with silver nitrate and albumen. The orthophosphates give a yellow precipitate with the former, while the pyro- and meta- phosphates give a white precipitate; and the metaphosphate gives an abundant precipitate with albumen, while the others give none.

Our knowledge of the various sodium phosphates is largely due to Graham (T. 1833, 253–284). The metaphosphates have been particularly examined by Maddrell (C. S. Mem. 3, 373).

Several highly-complicated phosphates not belonging to either of these classes are also known. Thus Fleitmann and Hanneberg (A. 65, 304–334) have obtained peculiar phosphates, one of which has the composition $Na_6P_4O_{13}$, by fusing tetra-sodium pyrophosphate with sodium monometaphosphate, and Filhol and Senderens (C. R. 93, 388) have obtained a phosphate of the composition $(NaHO)_3(P_2O_5)_2H_2O$ by adding soda to a solution of orthophosphoric acid until neutral to colour tests.

Three orthophosphates, respectively containing one, two, and three atoms of sodium in the molecule, are known.

Trisodium orthophosphate Na_3PO_4 is obtained by adding excess of caustic soda to hydrogen sodium phosphate, and crystallising to remove the free alkali. It may also be prepared by fusing hydrogen disodium phosphate with excess of soda and dissolving and crystallising. It crystallises in non-efflorescent six-sided prisms of the composition $Na_3PO_4.12H_2O$. According to Mohr (Am. S. [3] 14, 281), their sp. gr. at 17·5° is 2·5362. They fuse at about 77°; at 100° they lose eleven molecules, but they retain the last until the heat approaches redness.

Hydrogen disodium phosphate Na_2HPO_4 occurs in urine, and was at one time prepared from it under the name *sal mirabile perlatum*. It may be prepared by adding sodium carbonate to phosphoric acid until alkaline, and filtering, concentrating, and crystallising the solution.

It is usually prepared from the acid calcium phosphate made by the action of sulphuric acid on bone ash. For this purpose the hot solution is treated with sodium carbonate until effervescence ceases, and the hydrogen sodium phosphate thus produced is filtered from the precipitated tricalcium phosphate, and is concentrated and crystallised.

The salt crystallises in large, colourless, transparent monoclinic prisms of the composition $Na_2HPO_4.12H_2O$. They soon effloresce, and become opaque on exposure to the air.

They melt at 35° (Tilden, C. J. 45, 268), and have a sp. gr. of 1·5235 at 15° (Stolba, J. Ph. 97, 503). When dried over sulphuric acid, or heated for some time to 45°, they become anhydrous.

According to Poggiale (J. Ph. [3] 44, 273), 100 parts of water dissolve the following amounts of the anhydrous salt:—

0°	1·55	60°	55·29
10°	4·10	70°	68·72
20°	11·08	80°	81·29
30°	19·95	90°	95·02
40°	30·88	100°	108·20
50°	43·31	106·2°	114·43

The solution possesses a slightly alkaline reaction. When evaporated at 33°, it deposits monoclinic crystals of the composition

$$Na_2HPO_47H_2O.$$

Hydrogen disodium phosphate is used in certain photographic toning solutions, and to some extent in calico printing.

Dihydric sodium phosphate H_2NaPO_4 is obtained by adding phosphoric acid to a solution of hydrogen disodium phosphate until the solution ceases to precipitate barium chloride.

The salt crystallises in large trimetric crystals, of which two forms occur, each containing 4 molecules of water. It becomes anhydrous at 100°, and melts at about 204°. Many double orthophosphates containing sodium are known. Among them may be mentioned microcosmic salt $HNaNH_4PO_44H_2O$; sodium diammonium phosphate $Na(NH_4)_2PO_44H_2O$ (Melsmann, Ar. Ph. [2] 99, 138; Filhol a. Senderens, B. C. 1882, 641), and double phosphates of sodium and potassium (Filhol a. Senderens, *l.c.*), and of sodium and barium (De Schulten, C. R. 96, 706).

Hydrogen sodium ammonium phosphate $HNaNH_4PO_44H_2O$ occurs in urine and was well known as *microcosmic salt*, *fusible salt of urine*, or *essential salt of urine*, to the alchemists who used it as a source of phosphorus (*v.* Margraff, Miscellanea Berolinensia, 7, 341). It occurs as *stercorite* in guano (Herapath, C. J. 2, 70).

It is obtained by mixing solutions of 5 parts of hydrogen disodium phosphate and 2 parts of ammonium phosphate, or by mixing strong solutions of 6 or 7 parts of the sodium salt and 1 part of ammonium chloride:

$$Na_2HPO_4 + NH_4Cl = Na(NH_4)HPO_4 + NaCl.$$

It is re-crystallised from a solution containing a little ammonia, and is thus obtained free from sodium chloride.

Microcosmic salt crystallises in monoclinic prisms of sp. gr. 1·554 (Schiff, A. 112, 88). They effloresce slightly in dry air, and possess a saline, cooling taste. They are soluble in about 6 parts of cold and 1 part of hot water, but are insoluble in alcohol. The aqueous solution is alkaline, and evolves a part of its ammonia on evaporation.

When heated it melts and evolves water and ammonia, leaving sodium dihydrogen phosphate, from which the metaphosphate is obtained on further heating. The solvent action of the latter salt on many metallic oxides, and the characteristic colours obtained, has caused microcosmic salt to be largely used in blowpipe analysis.

Sodium pyrophosphates. Several of these salts are known. The normal pyrophosphate $Na_4P_2O_7$ is obtained as an anhydrous glass by heating hydrogen disodium phosphate to about 240°. It crystallises from water in monoclinic alkaline crystals of the composition $Na_4P_2O_7.10H_2O$. They have a sp. gr. of 1·7726 at 21° (Mohr, Am. S. [3] 14, 281) and melt at about 888° (Carnelley, C. J. 33, 278). When dried *in vacuo* over sulphuric acid, the salt becomes anhydrous, and has then a sp. gr. of 2·373 at 17° (Mohr, *l.c.*).

The aqueous solution is converted into the orthophosphate by boiling in presence of an acid, even acetic or phosphoric acid determining the change (Stromeyer, S. 58, 130 and 132). On account of the ease of its preparation it is used to prepare the soluble double pyrophosphates and the insoluble pyrophosphates. It is sometimes used medicinally instead of the orthophosphate.

The *disodium pyrophosphate* $Na_2H_2P_2O_7$ is obtained by heating dihydrogen sodium orthophosphate to 200°: $2H_2NaPO_4 = H_2Na_2P_2O_7 + H_2O$, or by dissolving the tetrasodium pyrophosphate in acetic acid and adding alcohol, which precipitates it as a white, crystalline powder. It is readily soluble in water, and possesses an alkaline reaction. Several double pyrophosphates containing sodium with potassium, ammonium, calcium, barium, magnesium, and other metals are known (*v.* Pohl, B. 6, 1465).

Sodium metaphosphates. These bodies form an interesting class, no less than five series of them having been shown to exist. They may be regarded as salts of polymeric or condensed metaphosphoric acids, and are respectively known as mono-, di-, tri-, tetra-, and hexametaphosphates. They are all soluble except the monometaphosphate, and have the following composition:—1. $NaPO_3$; 2. $Na_2P_2O_6.2H_2O$; 3. $Na_3P_3O_9.6H_2O$; 4. $Na_4P_4O_{12}.4H_2O$; 5. $Na_6P_6O_{18}$ (*v.* Maddrell, C. S. Mem. 3, 373; Graham, Phil. Trans. 1833, 253; Fleitmann, P. 78, 246 and 361; Fleitmann a. Hanneberg, A. 65, 304–334; Jarsein a. Thillot, B. 22, 654; Hautefeuille a. Margottel, C. R. 96, 849).

According to Tamman, there are three different insoluble sodium metaphosphates, and the salt hitherto called the di-metaphosphate has the composition $Na_3P_3O_9$, and that known as the trimetaphosphate the composition $Na_2P_2O_6$.

Sodium carbonate (*Carbonate of soda*) (inclusive of bicarbonate and of caustic soda).

Natural occurrence of the sodium carbonates. The sodium carbonates are found in many mineral waters (especially those of Aix-la-Chapelle, Karlsbad, and Vichy), in the 'natron lakes' of Hungary, Egypt, Central Africa, the Caucasian steppes, and in those of North and South America; also as efflorescences in such steppes, especially in the neighbourhood of natron lakes. These efflorescences or crusts are formed either by the partial or entire drying up in summer of such lakes or ponds, or else by the evaporation of subsoil moisture, more moisture (containing soda) being always brought to the surface by capillary action. The soda thus obtained in various places is known by the names *natron*, *trona*, or *urao*.[1] 'Urao,' according to Chatard (Bulletin No. 60, U.S. Geological Survey, 1887–1888), is essentially a carbonate of the formula $Na_2CO_3,NaHCO_3,2H_2O$, and is the most usual form of 'natural soda.'

The oldest-known occurrence of natural soda is that in Lower Egypt, where the natron lakes dry up in summer, leaving crusts of salt behind; in other places the 'trona' appears as efflorescences on the ground, consisting essentially of sodium sesquicarbonate, according to former assumptions, or rather, according to Chatard, of 'urao' mixed with other carbonates. Several thousands of tons of this article are yearly exported from Alexandria, principally for soapmaking. We omit the occurrence of natural soda in many other localities, where it is of no great technical importance, but we must mention the enormous quantities of soda found in the lakes and steppes of the 'Alkali Plain' and other parts of the great desert east and west of the Rocky Mountains. One of the most considerable of these occurrences is in Owen's Lake, in California, which, according to Chatard, contains per litre:

26·96	grms.	Na_2CO_3
5·71	„	$NaHCO_3$
11·08	„	Na_2SO_4
29·41	„	$NaCl$
3·14	„	KCl

with a little silica, alumina, calcium, magnesium, and boric acid. This lake contains from twenty to forty millions of tons of carbonate of soda, which is easily obtained in an almost pure state by solar evaporation in shallow ponds, and it is perhaps destined to be one of the great sources of soda for the world. Other large deposits of alkali are found in Wyoming and Nevada; but these contain too much sulphate, and are not easily worked for sodium carbonate.

Soda from the ashes of plants. Whilst most land plants contain in the soluble part of their ashes chiefly potassium carbonate and other potassium salts, there exist some 'soda plants,' growing on the sea-shore or near salt-springs, whose ashes furnish a very impure kind of soda, formerly very much used by soap-makers. Most of these plants belong to the family *Atripliceæ*—namely, the genera Atriplex, Chenopodium, Salsola, Salicornia, Kochia, &c. The plants growing in the sea itself, especially fucus, yield another kind of ashes, called 'kelp' in Scotland and 'varec' in Normandy, containing very little sodium carbonate, but a large quantity of potassium chloride and sulphate, along with a little iodate, which formerly was the only available source of iodine; in manufacturing this, 'kelp salt'—that is, sodium chloride containing some carbonate—was obtained as a by-product. The ashes from the real soda plants growing in Spain bear the commercial name 'barilla'; those from the south of France go by the names of 'blanquette,' 'salicor,' 'soude douce,' &c. The general name of these products is *vegetable soda*, but frequently *barilla* is used in the same sense.

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[1] Comp. Lunge's Manufacture of Sulphuric Acid and Alkali, ii. 287–291.

Vegetable soda, being simply fluxed ashes not purified by lixiviation, contains a large proportion of residue insoluble in water; the portion soluble in water contains sodium and potassium carbonate, sulphate, and chloride, along with small quantities of sulphides and thiosulphates formed by reduction from the sulphates; it is, moreover, frequently adulterated with a large quantity of common salt. In the analyses by Girardin, the proportion of sodium carbonate varies from 2 to 13·76 per cent. (Lunge, 2, 295).

In 1837 there were still 12,000 tons of barilla imported from Spain into England, in 1862 only 1,262 tons. A product of so little intrinsic value and of so variable a composition could not hold its ground, let it be ever so small, except owing to the ignorance and prejudices of some consumers.

Artificial soda.

Historical.[1] Only when Duhamel, in 1736, had demonstrated the identity of the base of common salt with that of 'mineral alkali,' as the natural soda then was called, was it possible to think of manufacturing soda artificially. But the problem was not actually approached till about 1775, when Scheele discovered that common salt could be partly converted into caustic soda by means of lead oxide. In the same year the French Academy of Science offered a prize for the solution of the problem of economically converting common salt into soda; and this was a stimulus to many inventors, only one of whom, Nicolas Leblanc, ultimately proved successful. His first experiments are said to have been made as far back as 1784; in 1789 his process was so far completed that he was able to submit it to the Duke of Orleans (whose domestic physician he was) in order to obtain the capital for carrying it out on a manufacturing scale. This led to several agreements in 1790, and, in 1791, to a patent which practically embodies all the principles of the Leblanc process as carried out to-day. About that time manufacturing operations were commenced at La Franciade, at St. Denis; but on the execution of the Duke of Orleans, in November, 1793, these works were closed, and in 1794 a decree of the Committee of *Salut Public* compelled Leblanc to give up his patent 'for the benefit of his country.' In spite of his reclamations, only the miserable sum of 600 fcs. was awarded to him as indemnification for his losses. In 1801 the works were given back to him, but he had no capital to start them with, so that he could not even compete with those works which had been in the meantime erected elsewhere, especially at Marseilles, in order to profit by Leblanc's invention. A committee, appointed to report upon his claims, ultimately, in 1806, made an award, but the sum was so small that Leblanc, in his despair, put an end to his life. That small sum was not even paid to his family.[1]

Even before Leblanc fell a victim to the ingratitude of his countrymen, and in the next succeeding years several alkali works employing his invention were founded in France in the same localities where that manufacture still flourishes. In England the first attempts at manufacturing artificial soda were made by W. S. Losh, at Walker, near Newcastle-on-Tyne, in 1806; the Leblanc process was tried there on a very small scale in 1814, and at St. Rollox in 1818. The enormous salt duty levied in England (30*l.* per ton) at that time practically prevented the establishment of alkali works. Immediately after its abolition in 1823 James Muspratt started his works near Liverpool, which for six years remained the only one in England, except a few small works on the Tyne. The small quantity of black ash then made in France and England contained only about 10 or 12 p.c. of alkali; Muspratt, however, from the first succeeded in making it of a strength of 24 p.c. of alkali, and in this form it was sold to the Liverpool soap makers to be used in lieu of kelp.[2] It was found when this black ash was exported that it quickly lost strength, and this led to the manufacture of sodium carbonate by lixiviation, evaporation of the liquor, and calcination of the residue.

Since that time the manufacture of soda-ash in England has principally developed itself in South Lancashire and on the banks of the Tyne; minor centres existing near Glasgow, and near Birmingham, &c. In these the Leblanc process has received a great many improvements, and it may be said that until the last ten or fifteen years or thereabouts England has stood at the head of this industry, not merely as far as the quantity of the article produced is concerned, but also with regard to its quality, and, to a great extent, to the perfection of the processes. In these latter respects, however, the French, and perhaps still more the German and Austrian, alkali manufacturers have recently also been prominent, and have introduced many important improvements in the Leblanc process. Still it cannot be doubted that the Leblanc process, a French invention, has been principally developed in England, while the ammonia process, an English invention, was first brought to a successful issue in Belgium and France.

The great drawback of the Leblanc process is the loss of all the sulphur introduced into it, most of which passes into the extremely objectionable form of 'tank waste,' and thus causes a great nuisance. This has induced very many inventors to make attempts at supplanting the Leblanc process by other processes. But for a long time none of these prospered, and the Leblanc process was the only one practically employed on a large scale. The manufacture of soda from cryolite, first started at Copenhagen on a very small scale in 1857, and afterwards principally carried on at Natrona near Pittsburg, in North America, from the necessity of the case was never a serious competition to the

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[1] Comp. Lunge's Alkali, ii. 296–308.

[1] Report of the Committee of the French Academy, May 31, 1856, and especially 'Nicolas Leblanc,' par Aug. Anastasi, Paris, 1884.

[2] E. K. Muspratt, S. C. I. 1886, 408.

Leblanc process. This process has, however, been supplanted to a great extent, and its very existence is now seriously threatened, by the ammonia-soda process, first invented by Dyar and Hemming, in 1838, who have practically laid down all its chemical principles. Although this process from the first roused a great deal of attention, and led to very numerous and partially very energetically pursued attempts on a manufacturing scale, in England, France, Germany, and Austria, it was reserved to Solvay, in Belgium, to introduce such mechanical improvements in this process that it became economically a rival to the Leblanc process, which it would indeed have entirely supplanted some time ago if the ammonia process permitted hydrochloric acid to be obtained as easily and cheaply as the Leblanc process. Solvay's works at Couillet, near Brussels, were started in 1863; but his principal improvements were made in 1872, and only then the ammonia process took its present rank.

General Remarks on the Manufacture of Soda.

The only raw material, offered by nature in inexhaustible abundance for the manufacture of both sodium and chlorine compounds, is sodium chloride, which, as rock-salt, forms whole geological strata, and which can be obtained very cheaply both from sea-water and from many brine springs. All other raw materials are of very little importance for that purpose; those which possibly contain as abundant a supply of sodium—namely, soda-felspar and certain other silicates—are decidedly not fit for the economical extraction of soda. As a source of chlorine, the magnesium chloride, produced in enormous quantities as an almost worthless by-product of the Strassfurt potash industry, is as yet only a future rival of sodium chloride, and is, in any case, only indirectly concerned in this question, in so far as it may influence the economical aspects of some soda processes.

In sodium chloride, Na and Cl are held together by a great force, represented by the number of thermal units produced in their combination—namely, 97,690 gram-units for one gram-molecule of NaCl(=58·5), or 195,380 gram-units for 2NaCl. Now, the corresponding figure for NaOH is only 102,030, and from this we may conclude that it is not possible to directly obtain NaOH from 2NaCl by mere heat, or in any other simple way, since we find it always very difficult to convert heat into latent (potential) chemical energy, whilst it is easy to convert such energy into heat, as is done in combustion and in many other chemical reactions. As a rule, chemical change can only take place if the thermal units represented by the formation of the new compound or compounds are superior to those of the original compound or compounds. In order to bring about changes of an inverse order, such as that which concerns us here, we have practically only two means at our command: either the employment of a physical force more potent than heat in overcoming the latent chemical energy—that is, electricity—or else, turning the difficulty by first applying some intermediate reaction which converts the original compound into one more easily split up by chemical means, aided by a proper temperature. This necessitates the employment of auxiliary substances, which sometimes are and sometimes are not recovered in the later stages of the process; sometimes new products are formed which contain one of the constituents, either of the original substance or of the auxiliary bodies in such a form that it seems, and frequently for a time actually is, economically impossible to recover the same. In every case such an indirect process entails a large expenditure of heat; for whenever the successive reactions are made alternately at higher and lower temperatures, the heat employed or given off in the first stage is nearly always entirely, or at least partially, lost before proceeding to the second stage.

For our present purpose, we shall pursue the course taken in converting sodium chloride into the commercial products: sodium carbonate (or hydrate) and chlorine (in the shape of bleaching powder, &c.). This can be done by the electric current, and at some future period this may become economically possible, but that object, although incessantly pursued, has not yet been practically achieved. It can also be done by the Leblanc process, proceeding as follows. An auxiliary substance, found in nature, and possessing a great store of chemical energy, is brought in—namely sulphur, in the shape of brimstone or pyrites. This is first converted into a compound, still possessing very much chemical energy—viz. sulphuric acid. Since the thermal units required to produce Na_2SO_4 (31,380) are superior to those required for 2NaCl (27,480), it is easy to effect the reaction:

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

The hydrochloric acid formed is itself a very useful product, but it would not nearly be utilised to the full extent in which it is produced in the Leblanc process if we did not bring in a further supply of chemical energy, in the shape of the active oxygen of MnO_2, which splits off free chlorine. In what way it is possible to recover the MnO_2, or to replace it entirely by other agencies, is shown in the article Chlorine. Here we must pursue the Na_2SO_4. This can be reduced by carbon to Na_2S, which is certainly an 'endothermic' reaction, but can be carried out by the application of external heat. Na_2S is a compound capable of easily combining, for instance with oxygen, and otherwise exhibiting great mobility. Its sulphur can be easily replaced by the radicle of carbonic acid, either by directly bringing it into contact with the latter (that is, $CO_2 + H_2O$), or by heating it with calcium carbonate, which is another auxiliary substance taken from the great storehouse of nature. We shall see further on that both sulphur and calcium carbonate can be recovered to a great extent, so that ultimately the splitting up of sodium chloride into soda and chlorine is almost entirely a question of the expenditure of fuel; but this has not been fully achieved until quite recently.

The only other successful process for manufacturing soda from sodium chloride is one which equally operates with an auxiliary substance—viz. ammonia. In this case the chain of reactions theoretically permits the whole, practically nearly all, of the ammonia to be recovered. But this favourable result is weighted with the drawback that the chlorine ultimately appears in the shape of calcium chloride, from which it can be set free only by other roundabout processes, too costly to compete with the simple way of preparing it from the hydrochloric acid obtained in the Leblanc process. In any case a very large amount of chemical energy, in the shape of coal, is required for that purpose.

Without entering into similar detail with other processes for splitting up NaCl, we may take it for certain that they must all make a sacrifice of chemical energy, and employ some intermediate body. They have all failed, either because the auxiliary substances employed could not be entirely recovered, or because that recovery was too expensive. In the following synopsis we do not aim at absolute completeness, but we shall mention all the more important proposals for manufacturing sodium carbonate or hydrate, whether actually carried out on a manufacturing scale or not.

ENUMERATION OF PROCESSES PROPOSED FOR MANUFACTURING SODA.[1]

A. From common salt without converting it into sodium sulphate.

Potash was used in the infancy of the manufacture of soda by Bergmann, Hahnemann, Losh, and others, at a time when the former alkali was less valuable than the latter, the reaction being $K_2CO_3 + 2NaCl = 2KCl + Na_2CO_3$.

Lime slightly decomposes common salt, as first noticed by Scheele. In 1782 Guyton de Morveau and Carny obtained a French patent for this process, which they actually worked for some time, of course with very little success.

Lead oxide. Scheele, in 1773, noticed that common salt is (partially) decomposed by lead oxide, caustic soda and lead oxychloride being formed:

$$2NaCl + 2PbO + H_2O = 2NaOH + PbO,PbCl_2.$$

This process was at first considered one of the most favourable for the manufacturing of soda, and was worked both in France and England, where many patents were taken for it. It was the process first employed by Losh at Walker-on-Tyne, at the same works where also one of the most recent patents belonging to this class, Bachet's, received a serious trial in 1870, but with hardly more success than formerly. The incompleteness of the reaction is the principal obstacle to this process. A new patent for it is Knab's (Eng. Pat. No. 3,082, of 1877). The Société Anonyme Lorraine Industrielle (Germ. Pat. 23,791) separates the caustic from the lead oxide by alcohol.

Romiquières (Eng. Pat. 14,977, 1888) dissolves finely-divided lead in caustic soda by means of a current of air. The solution of Na_2PbO_2 thus obtained is treated with NaCl, and thus two molecules of NaOH for each molecule previously employed are formed, $PbCl_2$ being precipitated.

Magnesia has been patented by W. Weldon (March 1, 1866) for the following reaction: $2NaCl + MgCO_3 + CO_2 + H_2O = 2NaHCO_3 + MgCl_2$. The inventor expected to obtain all the soda as bi-carbonate, and to decompose the $MgCl_2$ into MgO and HCl. It is hardly necessary to point out that both of these reactions are far too incomplete for practical use; recently the same process has been taken up by Engel for manufacturing potash from KCl, with rather more, but still not sufficient, success.

Sulphide of iron is used by Reynaud (Eng. Pat. 14,483, 1890), who heats it with NaCl, with the production of chlorine, sodium sulphate, and ferric oxide. This residue is mixed with coal and heated, producing a ferro-sodium-sulphide, which is treated by Blythe and Kopp's process (see below).

Oxalic acid and oxalates of ammonium and magnesium have been employed by various inventors. Their action is based on the slight solubility of the monosodium oxalate. The oxalic acid might, of course, be recovered. None of these agents seem ever to have been tried on a large scale.

Hydrofluoric acid was proposed by Weldon (in 1866), and

Hydrofluosilicic acid by many inventors, these acids forming very slightly soluble sodium salts. A factory, working on a patent by Karcher and Tessié du Motay, existed for some years up to 1870, near Saargemünd, and the process seems to have given better results than might have been anticipated; but the various reactions on which it is based are too incomplete for practical use. A French patent by Lefranc and Vivien (No. 208,878) describes the manufacture of hydrofluosilicic acid.

Calcium fluoride is employed by Brochon (French Pat. 208,754).

Alumina decomposes sodium chloride, in the presence of steam, at a very high temperature; this was utilised by Tilghman in 1847, and it has been taken up more vigorously since the discovery of native alumina in the mineral bauxite. Of course, sodium aluminate is formed, and is decomposed as in the manufacture of soda from cryolite (see below). But the temperature required for the above-mentioned decomposition is too high, and the vessels employed cannot be made to last. On this account the attempts of Gossage (1862), of Grüneberg and Vorster (1876), and of Lieber (1878) have had no practical results.

Clay, common salt, and water are employed by Kayser, Williams, and Young (Eng. Pat. 11,492, 1887). The mixture of these materials is moulded into bricks, and is heated in a current of superheated steam, when hydrochloric acid is given off. The insoluble compound remaining behind is crushed, and is fused with more soda, which produces an easily soluble compound, from which soda is to be extracted (!).

Silica and steam were employed as early as 1809 for decomposing common salt by Gay-Lussac and Thénard. This reaction was afterwards tried on a practical scale by Blanc and Bazille (1840), Fritzsche (1858) and others, especially by Gossage (1862), who brought sodium chloride in the state of vapour, along with steam, into contact with intensely heated quartz. The sodium silicate formed runs down in a fluid state. It is either used as such, or converted by CaO into NaOH, or by CO_2 into Na_2CO_3. This process was worked for some time, but the decomposition was too incomplete, the HCl was too difficult to condense, and the apparatus could not resist the intense heat.

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[1] Comp. Lunge's Alkali Manufacture, ii. p. 309 *et seq.*

Chromium oxide and steam has been patented by Swindells (1851), and Kessler (1867), but the reaction is quite incomplete. The process of Hargreaves and Robinson (1872), founded upon the employment of alkaline chromates, has not been any more successful.

Boric acid and steam have been patented by Margueritte (1855); boric acid alone by Garroway (Eng. Pat. 17,395, 1889).

Trimethylamine has been patented by Ortlieb and Müller, but evidently merely for the decomposition of potassium chloride.

Ammonium carbonate is the only substance by which common salt can be directly converted into soda with practical advantage. This process, first patented by Dyar and Hemming, in 1838, will be described at length further on.

Steam alone decomposes NaCl at a very high heat, and this reaction has been the subject of many patents, but unfortunately the reaction $NaCl + H_2O = NaOH + HCl$ proceeds only a very little way, otherwise this would be undoubtedly the simplest way of decomposing NaCl. It is, however, very unlikely that external heat alone can supply the energy required for bringing about the above reaction, which is strongly endothermic.

Sulphuric acid and coal, mixed with common salt, are supposed to produce soda (Robinson, Eng. Pat. 10,080 of 1884).

Barium or strontium sulphate are to be ignited with common salt in a current of superheated steam. This is supposed to produce caustic soda and hydrochloric acid (Bolton, Eng. Pat. 14,866, of 1884).

Magnesium sulphate (kieserite) is heated with sodium chloride and silica or clay in a current of air to 500° or 700°C. Chlorine is given off; sodium sulphate and magnesia remain behind (Townsend, Germ. Pat. 10,641).

The galvanic current has been employed for manufacturing soda and chlorine, in 1872 by Faure, in 1874 by Richardson and Grey, and by many other inventors. It can certainly effect the decomposition of common salt, but the action is a very slow one, and the cost of generating the current has hitherto been far greater than the cost of manufacturing soda in the ordinary way. If this cost could be very much reduced, by diminishing the great losses of energy in converting heat into electricity and the latter into chemical force, or if, in lieu of heat, very much cheaper sources of power could in future be employed to generate electricity, such processes would undoubtedly have a great chance of success. Patents for decomposing salt by electricity have been again taken out during the last few years by Wastchuk and Glouchoff (Germ. Pat. 10,039), Wollheim (Germ. Pat. 16,126), Spence and Watt (Eng. Pat. 1,630, 1882), Köpfner (Eng. Pat. 6,736, 1884), Marx (Germ. Pat. 46,318 and 57,670), Spilker and Löwe (Germ. Pat. 47,592, 49,627, and 55,172; Eng. Pat. 13,306, 1888), Parker and Robinson (Eng. Pat. 14,199, 1888), Greenwood (Eng. Pat. 14,239, 1888; 18,990, 1890; 2,019, 1891), Richardson (Eng. Pat. 2,296, 1890), Nahnsen (Eng. Pat. 11,699, 1890).[1]

SODA FROM SODIUM SULPHATE.

Without converting it into Sulphide.

By means of lime. In 1789 Delius proposed this agent, and many other chemists followed him; in 1865 Hunter added the action of pressure. But the change is extremely imperfect, as proved by Hill (C. N. 27, 165), and experiments made by the author have confirmed this.[1]

Caustic baryta easily and completely decomposes sodium sulphate, but it is and always will be much too dear for practical use, in spite of several patents having been taken out for this process.

Caustic strontia was proposed for a very ingenious round of reactions by Ungerer (D. P. J. 188, 140). But as this process is very complicated, and includes the intervention of ammonia, it is far simpler and cheaper to employ Dyar and Hemming's process. There is also an American patent for strontium compounds (No. 454,136) by G. H. Gray.

Calcium bicarbonate was patented in France by Pongowski (1872). Lunge (D. P. J. 243, 157) found that this causes no formation of sodium carbonate whatever.

Strontium carbonate is nearly always mentioned at the same time as

Barium carbonate. This has been tried in the dry way, by Kastner (1826) and Anthon (1840); in the wet way by many inventors, beginning with Kölreuter, in 1828. The reaction: $Na_2SO_4 + BaCO_3 = Na_2CO_3 + BaSO_4$ is, however, incomplete, whatever temperature may be employed, even with excess of $BaCO_3$. But the decomposition is quite complete when barium bicarbonate is employed, or much more simply and cheaply by passing a current of CO_2 into an agitated mixture of $BaCO_3$ and solution of Na_2SO_4, as patented by Lunge in 1866. This process would be practicable, if a cheap method of recovering the $BaCO_3$ from the $BaSO_4$ could be found. At present it cannot compete with the ammonia soda process. Bramley (Eng. Pat. 1,050, 1866) regenerates the barium carbonate from the sulphate, formed from the carbonate, by reducing the sulphate to BaS, then dissolving this in HCl, and treating the solution of $BaCl_2$ with hydrated magnesia and carbonic acid (a very hopeless process!).

Ammonium carbonates have been several times proposed for decomposing Na_2SO_4, first by Bower (1840). Recently, after the analogous process with NaCl had attained such complete success, the above has been again proposed, principally in order to recover the chlorine, as well as the soda, by interposing the manufacture of sodium sulphate and HCl. The most important of the processes in this line is that of Deacon and Hurter; it will be described later on in connection with the ammonia-soda process.

Alumina decomposes Na_2SO_4 in the presence of steam. This reaction, first proposed by Tilghman in 1847, furnishes sodium aluminate, which is easily decomposed by CO_2, Na_2CO_3 being formed and alumina being regenerated. In lieu of pure alumina, the mineral bauxite, found at Baux in the South of France, and in several other places, also at Irish Hill and Straid, County

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[1] Comp. also the researches of Lidoff and Tichriomiroff (C. C. 13, 747), Naudin and Bidet (Ber. 16, 2278), Hempel (Ber. 22, 2475).

[1] D. P. J. 238, 69; *cf.* also Bevan and Cross, D. P. J. 242, 137.

Antrim, can be employed. Several German patents by Löwig Brothers (No. 93 and 1,650 of 1877) describe this process, in which, however, the manufacture of hydrated alumina is the principal feature. A modification of the alumina process was proposed by Vogt and Figge (Germ. Pat. 31,675), another by Behnke (Germ. Pat. 7,256).

Silica decomposes Na_2SO_4, especially in the presence of coal, sodium silicate being formed, which is, indeed, one of the ways in which this compound is manufactured. It has been proposed to employ this as a soda-manufacturing process, by subsequently converting the sodium silicate into carbonate or hydrate.

Hydrofluoric acid is mentioned in Weldon's patents of March 1, 1866, which are quite impracticable.

Calcium bisulphite and sodium sulphate yield calcium sulphate and sodium bisulphite. By heating the latter SO_2 is given off; the residual Na_2SO_3 is converted by lime into NaOH and calcium sulphite (Gutzkow's Am. Pat. 198,293 of 1877).

A mixture of carbon dioxide and monoxide is supposed to decompose sodium sulphate at a red heat into carbonate and sulphurous acid (Kayser, Young and Williams, Eng. Pat. 7,355, 1885). This process is entirely useless, according to the investigation of Watson, Smith, and Hart (S. C. I. 1886, 643). It has been tried on a practical scale at the Hautmont works, in France, in an apparatus similar to that of Hargreaves and Robinson for the manufacture of sulphate of soda, as the reaction is a very slow one. The drawbacks found there were: that the mass crumbles to powder, which stops the passage of the gas; that it is very difficult to keep the temperature at the proper point; and that all the sulphur escapes in the shape of SO_2, too dilute for any utilisation (Lunge, Pariser Ausstellungsbericht, 1889, p. 15).

Crude phenol from coal-tar was proposed by Staveley (Eng. Pat. 17,657, 1887). He agitates it with milk of lime and treats the resulting solution of calcium phenate with sodium sulphate. Calcium sulphate is precipitated; the solution of sodium phenate is decomposed by CO_2 into sodium carbonate and free phenol, which is used over again. Comp. also Staveley's paper, S. C. I. 1888, 807. This process is ingenious, but no doubt impracticable, especially owing to the hardly avoidable loss of phenol.

Calcium acetate is employed by Frerichs (Eng. Pat. 9,293, 1890). As the sodium acetate formed is to be converted into carbonate by destructive distillation, that proposal need not be discussed here.

Calcium sulphydrate is employed by Haddock and Leith (*cf. infra*, sub. *Soda waste*); also by Simpson (Eng. Pat. 17,765, 1890) in the following way: Saltcake, nitre-cake, or the like are converted by $Ca(SH)_2$ into $CaSO_4$ and NaHS; this is carried on in closed vessels under a pressure of 60–80 lbs. per square inch. The clear liquor is decomposed by CO_2, and the H_2S set free is passed into milk of lime, in order to re-form the original calcium sulphydrate. The soda is precipitated as $NaHCO_3$. A special application of this process is made upon low-class phosphatic minerals, which are suspended in water and treated with H_2S, the $Ca(SH)_2$ in solution being employed as above, whilst the enriched phosphatic mineral remains behind.

Calcium phosphates are employed in another patent of Simpson's (Eng. Pat. 18,835, 1890). They are made to react with sodium sulphate; the sodium phosphate thus formed is converted by lime into caustic soda and calcium phosphate.

Soda from Sulphate, after converting it into Sulphide.

By heating sodium sulphate with coal a mixture of sulphide and carbonate is obtained, and this process has been proposed from a very early period down to 1839, among others by Berzelius, Gay-Lussac, Graham, and Liebig. It is, however, quite impracticable for soda-making, except as an intermediary for other processes, in the first instance

By adding calcium carbonate, which is Leblanc's process, and will be described at length further on.

Barium carbonate has been proposed by Reinar (1858), in lieu of calcium carbonate, but there is no advantage in this, and the cost is much too great.

Carbonic acid has been very often proposed for decomposing sodium sulphide. Very many patents have been taken out for this process, and many attempts have been made to carry it out in practice. We mention of the older processes only those of Hunt (1860), and of Weldon (1876 and 1877). In spite of the apparent simplicity of the reaction:

$$Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S,$$

which can be made practically complete, the process has hitherto always failed, for the following reasons: it is not at all easy to carry out the reduction of sodium sulphate to sulphide in such manner that no oxidised products remain behind or are re-formed on lixiviating the mass; furnaces made of brickwork are very strongly acted upon, and iron is altogether out of the question; the carbonic acid to be employed cannot be cheaply made in a pure state, but it is usually contaminated with some oxygen, and is mixed with a very large excess of nitrogen. The former causes great part of the Na_2S to be converted into thiosulphate in lieu of carbonate, and the latter makes the H_2S so dilute that its utilisation was formerly almost impossible. Recently this last difficulty has been obviated by the process of Claus (*cf.* the article AMMONIA), which deals with dilute H_2S, by burning its hydrogen into H_2S, and recovering the S as such. This would give much more chance of success to processes of this class, but it seems doubtful that they will ever compete with the Leblanc or the ammonia process. It has also been formerly overlooked that the reaction between Na_2S and CO_2 is not simply $Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S$, but that it is principally, although not entirely, thus:

$$Na_2S + 2CO_2 + H_2O = 2NaHCO_3 + H_2S.$$

Special apparatus for decomposing sodium sulphide solutions by CO_2 has been recently patented by Thompson (No. 10,900, 1887), Chance (No. 1,495, 1888), Wallis (No. 15,367, 1888), Parnell and Simpson (No. 19,023, 1888). Barrow (No. 17,528, 1888) describes an apparatus for dealing with the H_2S by means of a solution of $FeCl_3$ or $MnCl_2$.

Further on, in the section *Bicarbonate of soda*, we shall mention the process of Mathieson and Hawliczek for preparing bicarbonate from sulphide by CO_2.

Sodium bicarbonate decomposes Na_2S thus: $Na_2S + 2NaHCO_3 = 2Na_2CO_3 + H_2S$. This reaction has been several times patented as a soda-making process (first by Wilson in 1840), but it seems to have a chance of success only as a means of purifying the liquor of the Leblanc process from the Na_2S always contained therein, and even there the action is not instantaneous.

On the contrary, sodium sulphide cannot be completely decomposed by CO_2, except by employing such an excess of the latter that very much bicarbonate is formed; and sodium carbonate is partially decomposed by H_2S, with formation of Na_2S and $NaHCO_3$.

Alumina mixed with sodium sulphide is treated in a current of hot air by Liermann (1878); sodium aluminate is formed, and the gaseous products which escape are passed into a vitriol chamber.

Metallic oxides—such as copper, zinc, lead, iron or manganese oxide—have been very frequently proposed for decomposing Na_2S into a metallic sulphide and caustic soda. These proposals have hitherto mostly failed, first, on account of the difficulty of preparing Na_2S on a manufacturing scale; second, because in practice much more of an equivalent of the metallic oxide is required for effecting a complete decomposition of Na_2S; third, because the recovery of the metallic oxide from the sulphide is too costly, always entailing a loss of some of the metal, and never effecting a thorough utilisation of the sulphur. Such processes have been found more useful for purifying Leblanc's liquors from Na_2S. Still, new attempts are continually made in this way—*e.g.* by Lalande (Germ. Pat. 41,991 of 1887). Lalande's process (which employs zinc oxide) has been found to effect the desulphurisation very well when tried at the St. Gobain works, but the separation of the ZnS and the regeneration of ZnO were found to be too troublesome.

A new form of this kind of process, which seems to be more promising, has been invented by Ellershausen (Eng. Pat. 1,015, 9,112, 16,676, 1890). He first forms a 'ferrate of soda,' similar to Loewig's (p. 481), by heating carbonate of soda with ferric oxide; on filtering a solution of sodium sulphide through a layer of ferrate of soda, the sodium sulphide is entirely converted into sodium hydrate, which can be easily manufactured into commercial caustic soda. The sulphur is retained in the form of an insoluble ferrosodium-sulphide, to which Ellershausen gives the formula $Fe_2Na_2S_4$, and which retains one-sixth of the total soda. The success of this process would to a great extent depend on a proper recovery of soda, sulphur, and ferric oxide from that ferrosodium-sulphide.

Iron or iron oxides decompose Na_2S also at a red heat. Malherbe in 1778 proposed iron which was oxidised by the fire gases. Blythe and Kopp, in 1855, patented the use of iron oxides. Their process was tried on a large scale, but given up as useless; and this result has been confirmed by very extensive experiments on a manufacturing scale made by the author in 1865. There is a double sulphide formed in this process, the formula of which is stated by Stromeyer (A. 107, 233) $= Fe_2Na_2S_3$; this must be decomposed by CO_2, in order to yield Na_2CO_3 and FeS; but much H_2S escapes, and the FeS is much too impure to be burned for SO_2, as had been intended by Blythe and Kopp. The mass, moreover, contains much sodium thiosulphate and re-formed sulphate, and the furnace bottoms are very strongly acted upon, whatever material may be used for them. Altogether, this process (as well as some others employing ferric oxide in a different way, patented afterwards) does not offer any chance of success.

The preparation of sodium sulphide itself on a large scale has caused so many difficulties that many inventors, after spending a large amount of money and time upon it, have given up this task as hopeless. This was, for instance, the case with Weldon's patents of 1876 and 1877. It is, however, a fact that Ellershausen has succeeded in manufacturing comparatively very pure sodium sulphide in specially-constructed plain reverberatory furnaces, without any but very simple precautions. Esop (Zeitsch. f. angew. Chemie, 1889, 284) gives a detailed description of a furnace for that purpose.

The principal difficulties formerly encountered were, that the material of the furnaces or vessels is very much acted upon, and that the mass in cooling and lixiviating is partly oxidised again.

Gossage, Mathieson, and Hawliczek (Eng. Pat. 12,480 of 1886) seek to avoid this by employing a kind of cupola, in which sodium sulphate is intimately mixed with coke and heated. The sodium sulphate remains incorporated with the coke; the mixture, after having descended to the lower part of the cupola and having cooled down, is lixiviated, and the coke used over again. This does not seem to have answered its purpose, for the inventors propose later on (Eng. Pat. 3,218, 1888) to mix 40 p.c. common salt with the saltcake in order to avoid the destruction of the lining of the furnace.

A very ingenious process has been invented by G. E. Davis (Eng. Pat. 11,846, 1887). It begins with decomposing NaCl by SO_2, air, and steam, by the ordinary Hargreaves process (see below, *Sulphate of soda*). When this operation is completed and the sulphate is still hot, a current of 'water-gas' $(CO + H_2)$ is passed through the cylinders. The H_2 acts on Na_2SO_4, producing Na_2S and $4H_2O$, the latter passing on as steam with the CO, which is not changed, and the excess of hydrogen. When the conversion into Na_2S is complete, a current of CO_2 is passed over it; Na_2CO_3 is formed and H_2S escapes, which is burned, and furnishes SO_2 for the first stage of the process. The CO_2 is produced by bringing the mixture of CO and steam, formed in the previous operation, into contact with heated surfaces, whereby CO_2 and H_2 are formed. (Probably the reactions described here are too slow and incomplete to make the process pay.)

Helbig digests sodium sulphate with alkali waste and black ash in cylinders, provided with agitators and heated by steam; the final reaction is:

$$2CaS + Na_2SO_4 + Na_2CO_3 \\ = CaCO_3 + CaSO_4 + 2Na_2S.$$

The sodium sulphide is found in solution, is separated from the insoluble matter by filtration, and is evaporated to 32°Baumé; foreign salts present are fished out during the evaporation, and, on cooling, crystals of $Na_2S,9H_2O$ are deposited. Similar reactions, and at a lower temperature, are produced by mixing black ash and soda waste without any sodium sulphate. The crystalline sodium sulphide absorbs oxygen very slowly, possibly (as Helbig supposes) because it is free from caustic soda.

Pure sodium sulphide is also infusible, when heated in close vessels on which it has no chemical action (Weldon, S. C. I. 1882, 430).

Sodium sulphydrate is prepared by Trachsel (Eng. Pat. 3,406, 1886) by igniting an intimate mixture of the sulphates of sodium and barium or strontium with coal, and lixiviating with water. On boiling down, first baryta or strontia separates out, and the remaining solution contains principally NaSH, which is then decomposed by CO_2. Comp. also Maistre (French Pat. 208,472).

Barrow (Eng. Pat. 10,491, 1886) decomposes sodium sulphate by barium sulphide and oxide, obtained from barium sulphate by reduction with coal.

MANUFACTURE OF SODA FROM NITRATE OF SODA.

A very large quantity of sodium nitrate is indirectly converted into carbonate, inasmuch as it is first worked for nitric acid, and the residual acid sulphate ('nitre-cake') is worked up along with common salt in the ordinary decomposing pans. A considerable number of proposals have been made for making soda purposely from sodium nitrate, always, of course, with the condition of fully utilising the nitric acid as well. For some time artificial potassium nitrate was made by decomposing native nitrate of soda by *potassium carbonate*, chiefly in the impure form of carbonised 'vinasse,' from the manufacture of beet-root sugar; but this process has long been superseded by the use of Stassfurt potassium chloride.

Silica or *alumina* expel nitric acid from $NaNO_3$; so does *calcium carbonate*; in all cases the reaction takes place at such high temperatures that the nitric acid is decomposed, and although its re-composition can be effected by an excess of air and water, this costs too much to compete with the ordinary manufacture of nitric acid. The vessels employed are also corroded to an enormous extent. The advantage of obtaining the sodium in the shape of silicate, aluminate, or even hydrate cannot compensate for these drawbacks.

Ferric oxide is used by Bradburn (Eng. Pat. 6,710, 1889) to convert sodium nitrate (being the residue of Dunlop's chlorine process) into hydrate.

Fannie Brown has patented the very hopeless process of manufacturing carbonate of soda by igniting nitrate of soda with coal-dust (Eng. Pat. 11,008 and 11,009, 1884). Freda and Patroni have taken out a French patent (No. 206,298) for the same process.

MANUFACTURE OF SODA FROM FELSPAR.

Soda felspar has been several times proposed for manufacturing soda—*e.g.* by Ward and Wynants (1857 and 1864), who heated it with fluorspar, chalk, and lime; but this process has been found far too costly even for potash, and is not likely ever to answer for soda.

MANUFACTURE OF SODA FROM CRYOLITE.

This mineral is found mainly in one locality—namely, the bay of Evigtok, in South Greenland, where it was discovered by whalers, and again by Giesecké (1806-1813). Since 1849 it has become of some importance, because Professor Julius Thomsen, of Copenhagen, proved it to be easily decomposable by lime, and to yield very pure soda and alumina. It was first worked upon a large scale in 1854, and several factories were erected for this purpose in various parts of Europe, but since 1865 the Pennsylvania Salt Manufacturing Company at Natrona, near Pittsburg, has obtained the control of nearly all the mineral got (about 6,000 or 7,000 tons per annum), so that hardly any soda is made from it elsewhere.

Cryolite is a double fluoride of aluminium and sodium, of the formula $Al_2F_6,6NaF$; in the pure state it contains 12·85 Al, 32·78 Na, 54·37 F, corresponding to 24·23 Al_2O_3 and 44·17 Na_2O, but as it comes into trade it usually contains about 15 p.c. of impurities (galena, pyrites, fluorspar, limespar). It is a snow-white mineral, easily fusible, and soluble in concentrated sulphuric acid, but insoluble in hydrochloric acid.

Thomsen's process for working it up (which is the only one carried out in practice) consists in igniting it with calcium carbonate, when CO_2 escapes and soluble sodium aluminate, with insoluble calcium fluoride, remain behind:

$$Al_2F_6,6NaF + 6CaCO_3$$
$$= Al_2O_3,3Na_2O + 6CaF_2 + 6CO_2.$$

Finely-ground cryolite (100 parts) is intimately mixed with 150 parts of ground chalk, and some of the impure CaF_2 obtained in the process itself is added to the mixture, which causes it to decompose more completely and greatly increases the yield of valuable products. The mass must be spread in a thin layer, and must be heated to a red heat, but short of being fluxed, which would cause an imperfect decomposition. This is done in furnaces specially constructed by Thomsen for this purpose, which finish each charge of 9½ cwt. in two hours (*cf.* Lunge's Alkali, iii. p. 55).

The furnace charge is put, while hot, into the lixiviating tanks, and is methodically washed. The residue from this operation is an impure calcium fluoride (containing 62 p.c. CaF_2, 12 p.c. $CaCO_3$, 5·6 p.c. CaO, &c.). It is used for making bottle glass, for enamelling stone ware, as a metallurgical flux, &c. The solution of sodium aluminate obtained, which tests from 48°–60° Tw., is decomposed in revolving cylinders, or in vessels provided with agitators, by the crude carbonic acid given off by a lime kiln.

The final result of the decomposition is stated thus:

$$Al_2O_3,3Na_2O + 3CO_2 + 3H_2O$$
$$= Al_2(OH)_6 + 3Na_2CO_3;$$

but in reality a compound of 45 p.c. alumina, 20 p.c. sodium carbonate, and 35 p.c. water is precipitated in a granular state, and must be freed from soda by long washing with hot water. This is carried on till the aluminium hydrate contains only 2 p.c. of soda. Most of it is converted into aluminium sulphate by dissolving it in dilute sulphuric acid at 90°C., and boiling down the solution in copper pans to the consistency of treacle; it is then poured into moulds and solidifies on cooling. The richest commercial article contains 20 p.c. Al_2O_3.

The solution produced in the precipitating vessels is boiled down to 66°Tw., and on cooling yields a crop of extremely pure soda crystals, containing hardly more than ¼ p.c. of foreign salts. The mother-liquors are so pure that they can always be taken back again into the process.

The Manufacture of Soda by the Leblanc Process.

The history of this process has been briefly mentioned above. It consists in heating a mixture of sodium sulphate, calcium carbonate, and coal till the mass has fluxed and attained a certain degree of decomposition. It is then called 'black ash,' and the batches drawn out of the furnace are frequently called 'balls.' Black ash is a very complex mixture of substances, which undergoes a somewhat rapid change by the action of the air. It is separated by the action of water ('lixiviation') into a residue—'tank waste,' 'alkali waste,' or 'soda waste'—and a solution containing the soda chiefly in the state of carbonate, along with some hydrate and a large number of impurities. From this either the commercial sodium carbonate ('soda ash') or the commercial hydrate ('caustic soda') is prepared by operations to be described below.

The reaction taking place in the black ash furnace has been interpreted by various theories. The matter is complicated, not merely by the large number of substances found in black ash, but also by the fact that, in order to fully decompose the sodium sulphate, an excess of calcium carbonate and coal must of necessity be employed. Taking an average of the many mixtures found in practice, we may assume that with 100 parts of pure Na_2SO_4 usually as nearly as possible 100 parts of pure $CaCO_3$ and 40 of pure C are employed—that is, to 1 molecule of Na_2SO_4 1·42 molecules of $CaCO_3$ and 4·73 of C; or, say, 1½ of $CaCO_3$ and 4½ of C; and the older theories, in fact, assumed those proportions to represent the number of molecules entering into action, without taking the fact into account that in a case like the black ash process, where the mixture never enters into complete fusion and the ingredients are never absolutely mixed with one another, the decomposition of the most valuable portion, the Na_2SO_4, can be brought about only by a mechanical *excess* of the other ingredients, which ensures that every portion of the Na_2SO_4 comes into contact with them.

Apart from this oversight, the first theory of the black ash process—that of Dumas (1830)—was based on two erroneous assumptions, namely, that CaS is soluble in water (confounding the compound $Ca(SH)_2$ with CaS, as was natural at that time), and that there exists in black ash an insoluble calcium oxysulphide, 2CaS,CaO (already assumed by Thénard). Believing that the action of water must cause CaS at once to act upon Na_2CO_3, Dumas thinks that this is prevented by the formation of 2CaS,CaO, and he represents the black ash process in this way:

$$2Na_2SO_4 + 3CaCO_3 + 9C$$
$$= 2Na_2CO_3 + CaO,2CaS + 10CO.$$

This would require for 100 Na_2SO_4: 105·6 $CaCO_3$, and 38 pure C—quantities decidedly in excess of those found sufficient at many alkali works for *completely* decomposing the saltcake, which fact alone would refute Dumas's theory.

That theory, further, but not very essentially, modified by Unger, Brown, P. W. Hofmann, and E. Kopp, was almost universally adopted until Kynaston, Gossage, and Scheurer-Kestner (1858–1867) exposed its fallacy by proving the nonexistence of calcium oxysulphide in black ash, and by other reasons equally cogent. They also pronounced against the theory that the principal oxide of carbon formed is CO, not CO_2—a theory upheld by Dubrunfant, and later on by Mactear, but decidedly refuted by the extensive investigations of Kolb (A. Ch. [4] 7, 118), and by laboratory experiments made by Lunge and Fischer.[1]

As the final result of the prolonged controversy on these points, of the large-scale experiments of Scheurer-Kestner and Kolb, and of the personal observations and experiments of the author, the theory of the black ash process may be stated as follows: the principal reaction going on is ultimately $Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2$. It is, however, extremely probable that this takes place in two stages, the first being the reduction of sodium sulphate by carbon to sulphide; the second being a mutual decomposition of the latter with calcium carbonate:

$$(1)\ Na_2SO_4 + 2C = 2CO_2 + Na_2S.$$
$$(2)\ Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

Nearly all the Na_2S is at once acted upon by $CaCO_3$ immediately after its formation, so that there is at no time any considerable proportion of it present, except in the case of abnormal work.

The above equations would require for 100 parts of pure Na_2SO_4 only 70·42 pure $CaCO_3$ and 16·9 pure C. One reason why much more of the two last ingredients must be employed for decomposing the whole of the Na_2SO_4 has been stated above, but there is another reason for it as well. In order to lixiviate the melted mass, it must have a certain degree of porosity, and must, moreover, be further disintegrated during the treatment with water. Without this, the lixiviation would require too much time, too high a temperature, and too great dilution of the liquor, and would thus produce a very inferior liquor, as well as a bad yield of soda. The above condition is practically attained by employing an excess of limestone and coal, which in the last stage of the process, when the temperature is at its highest, react as follows: $CaCO_3 + C = CaO + 2CO$.

The carbon monoxide, which is formed at a period when the mass has become pasty, causes it to become honeycombed, like the dough in a fermenting loaf of bread. The CO is actually seen escaping at this stage, and burning with a flame tinged yellow by sodium. The caustic lime remains behind, and afterwards, on being hydrated, causes the balls to swell up and burst, as well before as during the lixiviation. A further excess of limestone and coal, which ought not to be too great, produces greater porosity of the black ash in a purely mechanical way, since they are not fused like the remainder of the mass. Lastly, some portion of the coal is unavoidably burned before it can enter into action. All these reasons fully explain the necessity of employing an excess of limestone and coal; but it is impossible to embody this in a chemical formula, as has been attempted by Scheurer-Kestner, seeing that such excess acts merely in a mechanical way, and actually differs very much in different works.

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[1] Compare the complete discussion of the various publications on the theory of the black ash process in Lunge's Alkali, ii. 427–441.

It is hardly necessary to say that many subsidiary reactions take place at the same time; but these have nothing to do with the theory of the black-ash process, and merely explain the occurrence of the impurities always found accompanying the two principal products, sodium carbonate and calcium sulphide.

Description of the Black-ash Process.

Raw Materials.

Sodium sulphate (*saltcake*). This is nearly always obtained by the decomposition of common salt by sulphuric acid, or else by Hargreaves and Robinson's direct process from common salt, pyrites kiln gases, and air (*cf. Sodium sulphate*).

The saltcake for alkali-making should be a white or yellowish powder containing none but porous, friable lumps, but no fluxed pieces, which nearly always inclose some raw salt and decompose badly in the black ash furnace. Red ('foxy') saltcake does not yield good soda either; its colour indicates an excess of heat in calcining the saltcake.

Good, strong soda cannot be made with saltcake containing more than 0·5 p.c. of undecomposed NaCl, and 1 to 1·5 of 'free acid' (calculated as SO_3, and including bisulphate, pyrosulphate, ferric sulphate, &c.).

Good commercial saltcake contains 96 to 97 p.c. of real Na_2SO_4; that made with a large proportion of 'nitre cake' is generally unequal in quality, unless the nitre cake has been ground and carefully mixed with the salt in the decomposing pan. Fresh saltcake does not act so well in the black ash furnace as that which has been warehoused for some time, in which case a more thorough reaction between the undecomposed NaCl and the $NaHSO_4$ takes place.

Calcium carbonate. Both limestone and chalk are employed—of course, the purer the better. Magnesian limestone cannot be used, and limestone or chalk containing much silica causes a great loss of soda in the insoluble state. The chalk ought to be dried, and both it and the limestone ought to be crushed by rollers or edge runners to the size of a pea or a bean.

The Tyneside works mostly use the chalk brought down from the Medway by colliers as ballast. The Lancashire works employ mostly Buxton limestone, which works more easily in the furnaces than does chalk, and requires less heat for the 'balling' process.

Most of the caustic soda works employ the lime mud obtained in causticising the liquors by lime to replace part of the limestone in the black ash mixture.

Sometimes part (up to 15 p.c.) of the limestone is replaced by desulphurised soda waste from Mond's process; and this should take place to a very much larger extent by the calcium carbonate recovered by Chance's process for working up alkali waste (*v. infra*).

Coal. The quality of the coal employed for the black ash mixture is of great importance. It ought to contain as little ashes as possible, and this is more difficult with the small coal or 'slack' generally used than with lump coal, which is, however, too dear for this purpose. Even after washing, such small coal rarely contains less than 5 p.c. of ash; 6 p.c. is the maximum tolerated by some German alkali works; but in England 'slack' containing up to 8 p.c. ash is considered as very good for mixing. The coal ashes, consisting principally of aluminium and calcium silicates and ferric oxide, cause the formation of insoluble double silicates, which lock up a considerable portion of soda in a non-available form. The more ashes the mixing-coal contains, the less soda ash will be obtained with it.

The small quantity of pyrites usually contained in coals is of no great consequence for the black ash process. The 'volatile sulphur' in ordinary mixing-coal varies from 0·6 to 1·65 p.c.

It is not quite decided whether bituminous or 'dry' coal is preferable for mixing; but the balance of opinion is in favour of coal yielding a large proportion of fixed residue—that is, less bituminous matter—and it is certain that the quantity required in mixing is proportionate to the 'fixed' carbon of the coal.

Leblanc himself employed wood charcoal, which is now excluded by its price. Good lignite or crushed coke, if otherwise pure, can be very well employed in mixing. In any case very much care must be taken to decide by preliminary trials on a working scale whether a certain description of coal will answer for soda-making or not, as the whole success of the operation depends upon this, and analyses cannot entirely decide this point beforehand.

The nitrogen contained in coal, which varies from 0·5 to 1·75 p.c., gives rise to the formation of cyanides, part of which are converted into cyanate by the oxidising action of the flame. The moisture of the air decomposes the cyanate, with formation of ammonia, which is evolved during the cooling of the balls. But another portion of the cyanide remains behind, and is, during the lixiviation, converted into ferrocyanide, which afterwards causes much trouble (see further on).

J. Pattinson (in Trans. Newcastle Chem. Soc. 4, 183) gives analyses of nine descriptions of mixing-coal as used on the Tyne. That described as 'good' contains, in 100 parts, 61·19 to 66·45 fixed carbon, 25·27 to 27·35 bituminous substances, 0·6 to 1·47 volatile sulphur, 0·1 to 0·3 sulphur in ashes, 4·8 to 8·32 ashes, and 1·01 to 1·67 moisture. 'Inferior' mixing-coal contains only 56 to 58·8 fixed carbon, and 12·56 to 14·22 ashes.

Mixing-coal acts all the better the more finely divided it is; it is, however, rarely ground by itself, especially as it is mostly employed in the state of 'smalls' or 'slack,' but is only screened and roughly mixed with the other materials. At some works all the materials of a charge, after being weighed out, are passed through crushing-rolls, which have the action of both comminuting and intimately mixing them; and this is, no doubt, the proper way to obtain a good result.

The proportions in which the materials are mixed naturally vary with their quality, the amount of moisture, &c. Leblanc's original proportions: 100 saltcake, 100 chalk, 50 charcoal, are very nearly identical with those now in use in hand-furnaces. With 100 saltcake, rarely more than 100 limestone or dry chalk are used now. For mechanical black ash furnaces, where the charges are better mixed during the operation, somewhat less limestone may be employed, but it is not safe to go below 90 parts to 100 sulphate, otherwise the decomposition is likely to be imperfect, and weak, discoloured soda ash will be the result.

On the other hand, it cannot be doubted that any excess of limestone tends to produce a loss of soda in the shape of insoluble compounds. Such a loss had been long known to exist; it had been pointed out by Hargreaves (C. N. 1867, 15, 218, 232) and by Kynaston (C. J. 11, 135), who, however, attributed it to its sodium aluminium silicates. C. R. A. Wright (ibid. 1867, 20, 407; C. N. 16, 259) proved the practical importance of this loss, which he believed might partly be due to the formation of a sodium-calcium carbonate. This was more distinctly proved by Scheurer-Kestner, in 1872 (C. R. 75, 1,184), who showed that in reality any augmentation of the limestone in black ash mixing leads to a reduction of the yield of available soda. The hypothetical insoluble sodium-calcium carbonate was prepared artificially by Watson Smith and Liddle (Proc. Lit. and Phil. Soc. Manchester, 20, 24; C. N. 42, 243; 43, 7), and it was about the same time actually discovered, as an incrustation on settling tanks for soda liquor, by Reidemeister (Chem. Indust. 1881, 75), and identified by Rammelsberg with the mineral gay-lussite, $Na_2CO_3,CaCO_3,5H_2O$ (W. J. 1881, 271).

The quantity of coal for mixing is best kept as low as is compatible with good work. Some French makers use as little as 30 parts of coal to 100 of saltcake, and 40 to 45 of good coal is certainly sufficient; but in England usually much more (50 to 60 or even 70 parts) is employed, partly because it is considered imperative that each furnace should 'boil down its own liquor.' Those Continental manufacturers who use less mixing-coals do their boiling down as well by carefully utilising all the heat, and by using less mixing-coal they not only save the price of the difference, but they, moreover, profess to get better black ash, containing less cyanide and less caustic. The theory of black ash making, as we have seen above, requires only 70·4 $CaCO_3$ and 16·9 C to 100 Na_2SO_4; in practice 90 $CaCO_3$ and 32 C = about 40 coal ought to suffice for the unavoidable excess required to make the decomposition perfect and to keep the balls 'open,' including the CaO which should be present to promote the lixiviation, in consequence of bursting the pieces by the formation of $Ca(OH)_2$. Usually, however, more limestone and coal is employed, so that the mixture more nearly approaches the proportions of 100 saltcake, 100 limestone, and 50 (or upwards) coal.

The special features of some mixtures for revolving ball furnaces, especially the Mactear process and the Péchiney-Weldon process, will be mentioned later on.

The Black Ash Furnaces.

The furnaces in which the Leblanc process is carried out are either worked by hand or mechanically. The former class is, of course, that which was originally employed, and on the Continent it is even now more largely employed than mechanical furnaces, whilst in Great Britain the latter class is now prevalent at all larger alkali works.

The hand-worked furnaces are generally made larger in France than in England, and calculated for a much heavier charge; but these heavy charges cannot be easily worked through quite evenly without overheating them; the labour required for a certain weight of charge is no less, but rather more, than with the smaller type of furnaces used in England, and it is very doubtful whether the former offer any more economy in fuel. For these reasons the smaller English ball furnaces have replaced the larger type entirely in Germany, and partially even in France.

All black ash furnaces are so arranged that their waste heat is utilised for the boiling-down of liquor, sometimes also for other purposes, as calcining the ash.

There is, of course, some difference in the shape of the black ash furnace at different works; altogether the type of furnaces as used in Lancashire somewhat differs from the Tyneside type, but those variations only refer to less essential details, and it will suffice to give a description of the usual Tyneside ball furnace, which is very substantially built and easy to work, with working-drawings, having the dimensions indicated in metrical measure.

The diagrams (figs. 28 to 33) also comprise a boiling-down pan, such as is always attached to those furnaces; but in other localties the fire is conducted below, not above, the pan, as will be seen hereafter.

Fig. 28 is a sectional plan along line A B of fig. 29, passing through the hollow fire-bridge, but showing the beds and the pan from the top; fig. 29 is a sectional elevation along line C D of the plan; fig. 30 a front elevation, showing only the fire-cave and the drainer in section; fig. 31 a cross section along E F; fig. 32 another along G H, both looking towards the fire-bridge; fig. 33 a section through the pan. Such a furnace works off a 3-cwt. charge of saltcake in 45 to 50 minutes, so that with the necessary pauses for cleaning the fire, &c., 24 to 27 balls are made daily. *a* is the fireplace, provided with wrought-iron grate-bars; the bar *b* assists in poking up the fire from below from the fire-cave *c*. (Such 'cave-fires' are said to consume less coals than fireplaces with their ash-pits at the level of the floor, by the greater facility they offer for attending to the fire.) At *d* the fireplace is stepped backwards, so that the flame ranges all over the bridge *e*. The latter must be very carefully and strongly built of the best fire-bricks procurable, in which case it will last about three months. It is $2\frac{1}{2}$ to $3\frac{1}{4}$ feet wide, and on the Tyne is always made hollow. A cast-iron bridge plate *f*, $1\frac{1}{2}$ to 2 inches thick, prevents the charge from fluxing through the bridge; it must be protected against overheating

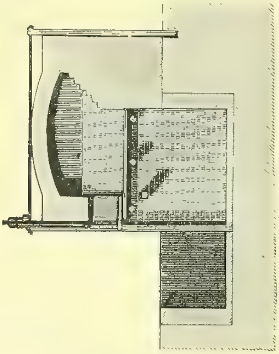
FIG. 31.

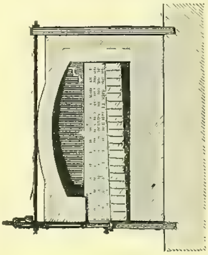
FIG. 32.

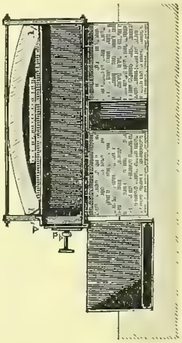
FIG. 33.

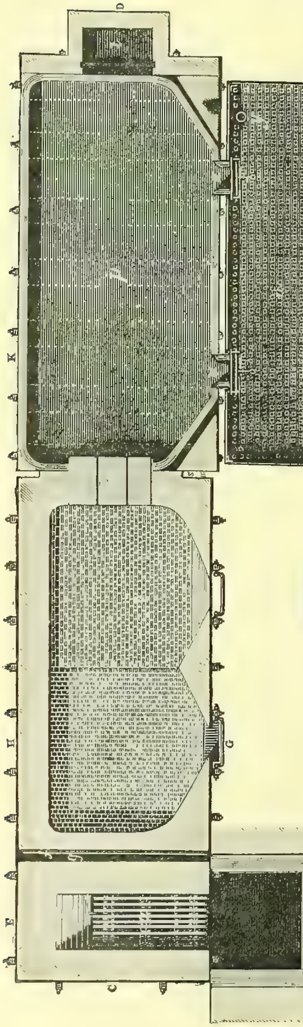
FIG. 28.

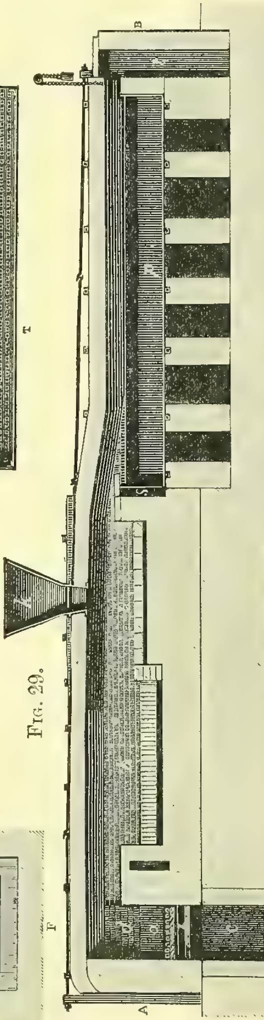
FIG. 29.

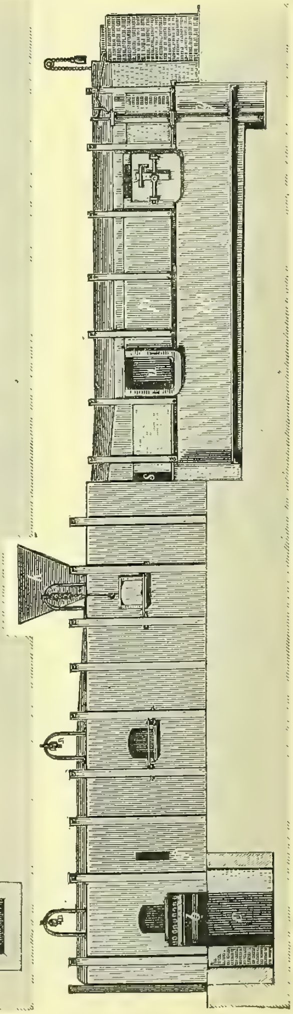
FIG. 30.

by an air channel *g*, open at each end. *h* and *i* are the two furnace-beds. The charge is put through a hopper *k* or else through the door, on the back bed *i*, which is 3 inches higher than the front bed *h*; to this the charge is transferred, when it is empty, in order to be finished and drawn out through its door. Sometimes three-bedded furnaces are met with. The front bed *h* is made of bricks on end, that is 9 inches deep, and is set upon a layer of ground chalk or fireclay, to isolate it from the foundation. The bricks are set dry, as closely together as possible (preferably grinding them upon one another, so as to minimise the width of the joints), and are grouted on the top with a thin paste of fireclay. The long joints are made to run towards the door, and the whole bed is made to slope about 2 inches that way, in order to facilitate the working of the tools. The back bed *i* is made of bricks on edge (*i.e.* 4½ inches high). The diagrams show how these beds are made within fire-brick 9-inch walls, so shaped that the tools can easily reach every part of the beds, and leave no dead corners. The front or working-bed, even if made of the best material and with the greatest care, rarely lasts longer than five months.

On the Tyne the furnaces are cased in solid cast-iron plates, tied together by upright binders and tie-rods; but in Lancashire the plates are frequently replaced by the less substantial plan of simple straps of wrought iron, 3 to 6 inches broad and ⅝ inch thick. The ends of the tie-rods are tightened up by screws and nuts, or else by loops and wedges.

In front of the working-doors there are special door plates and supporting-rods for the tools. The doors are best closed by fire-clay slabs, surrounded by an iron frame, and hung from a standard with chain, pulley, and balance-weight.

Adjoining the furnace, but separated from it by an air-channel *s*, is the boiling-down pan *p*, made of sheet iron ⅜ inch thick, preferably with counter-sunk rivets. There ought to be no joint running the long way of the pan, but all the plates ought to be in one piece from back to front. The shape of the pan is such that all its contents can be easily drawn out. These pans are made with two doors, or preferably somewhat longer than shown here (say 20 feet), and then with three doors. Round the top an angle-iron runs inside the pan, partly for stiffening it, and partly as an abutment for the arch, unless a special angle-bar *r* is provided for this purpose. The fire-clay slabs *o* protect the front pan edge from the fire. At the other end the flue *t* conveys the waste gases to the main flue, or else to some place where their heat is to be further utilised. The pan rests on pillars *qq*, so that it can be inspected from the bottom at any time, and any leaks can be discovered at once. The doors *u* are arranged in such a way that the whole contents of the pan can be drawn out into the drainer *w*, placed in front, while the pan is working. The doors are pressed against the angle-iron running round the edge of the openings, by means of a cross bar and screw bolts. Loose sheet-iron covers *v'* close the upper part of the openings, but allow inspection of the inner part at any time.

The *salt-drainer w* has a perforated false bottom, with holes ⅛ or ⅐ inch wide, resting on a framework of angle and T bars. The true bottom slopes to one side, and ends in a well in which is placed the liquor pump *y*.

The work in the black-ash furnace is carried on as follows: The mixture is put on the back bed, where it is levelled, and during its stay there is twice turned over, in order to dry it and heat it up. When the charge in the front bed has been drawn out the fire is allowed to play on the empty bed for a little while to make it properly hot, and then the previously heated charge is pushed over from the back bed by means of the working doors. Sometimes a portion of the ball is left a little longer on the back bed ('splitting a ball'). As soon as it is empty a fresh charge is put in. The principal work, of course, goes on on the front bed, which is heated to at least the melting-point of silver. F. Fischer (Berl. Ber. 10, 1,559) found the temperature of a Hanover ball furnace to range from 713°C. (just after charging) to 932°C. (before drawing); but in England, where the furnaces are made to do more work, they must be worked somewhat hotter, probably about 1,000°C. Soon after the mixture has been put on the front bed, the saltcake at the top begins to soften, and so far as it is converted into Na_2S it fuses completely. The furnaceman must now turn over the mass with his 'paddle' or 'slice,' so as to mix it up thoroughly, and to gradually raise it evenly to the proper temperature by moving the upper portions towards the bottom, and fetching up those lying on the bed. This turning over, which should not occupy more than a few minutes, is repeated twice more, leaving each time an interval of ten minutes, during which the working door is closed and the heat gets up again. The outside ends of the 'paddles,' 'rakes,' and other tools are supported by chains, and that part of the handles which is immediately in front of the working door rests on iron bars covered with waggon grease, in order to facilitate that very exhausting work.

About 30 to 40 minutes from the start the mass has become sufficiently liquid; but it is only a thin paste, never in the state of a real liquid, so that it does not run out at the door. The furnaceman now changes his paddle for a rake, with which he mixes the mass most thoroughly, and gradually draws it to the door. At this stage a great number of gas bubbles are seen to escape, which gives the mass an appearance of boiling; these bubbles do not burn, as they consist of CO_2, the principal reaction taking place now, of which CO_2 is the gaseous product (see above). Shortly after the mass, which had reached its thinnest stage, becomes stiffer, evidently because the Na_2S has been converted into the less fusible Na_2CO_3, and now numerous small jets of flame burst from the pasty mass. The men call them 'candles' or 'pipes.' They are caused by CO being formed now (see above), and burning away, the flame being tinged yellow by the soda. When they appear (*not* when they cease, as stated in some treatises), it is very nearly time for drawing out the balls. The man rakes it up very thoroughly, gradually works it towards the door, in front of which he had previously placed the iron 'bogie,' and then as quickly as possibly pulls the ball out. If the operation has been a good one, the ball will swell up in the bogie like a fermenting loaf of bread, and numerous 'candles' will still burst out of it. In reality, the reaction is only finished here, and should be promoted by stirring the ball in the bogies. If it has been heated too long, or else too short a time, it will be 'thin'; it will then not rise in the bogie, and few or no 'candles' will issue from it. Burnt balls contain much Na_2S, underheated balls much Na_2SO_4. At the finish the temperature ought to be the highest, but its action ought to be only short.

The making of black ash, although it can be learned by a somewhat intelligent and sufficiently strong man in a few weeks' time, is extremely heavy work, and requires constant checking on the part of foremen and chemists. The men are always paid by the piece, and are not allowed anything for bad balls.

The consumption of fuel for ordinary black ash furnaces varies from 13 cwt. of coal per ton of sulphate down to 10 cwt., both excluding unusually bad or good work. This includes, of course, all the fire for boiling down the liquor, but it does not include the mixing-coal. With the very best appliances and the greatest care the coal for firing and mixing together may be brought down to 14 cwt. per ton of sulphate, but this is exceptionally good work.

Even by employing the waste gases of the black ash furnaces for evaporating the liquors their heat is nothing like fully utilised. At some works they use it further for raising steam, or for drying soda ash to a certain point, but even then the gases escaping into the chimney have a temperature exceeding 500°C. An attempt made at better utilising their heat by means of Perkin's high-pressure water tubes, as described by Hurter (S. C. I. 1884, p. 67) did not turn out successful, owing to mechanical difficulties caused by the expansion of the tubes.

F. Fischer (D. P. J. 234, 306) has examined the gases from hand-worked black ash furnaces at all stages of the work, in two different works. He found in one case from 17·8 to 23·1 p.c. CO_2 and 2·1 to 8·6 p.c. O; in the other case 11·0 to 22·7 CO_2 and 2·8 to 11·4 O, but never any carbon monoxide. Whether the latter holds good of revolving furnaces as well, is still uncertain.

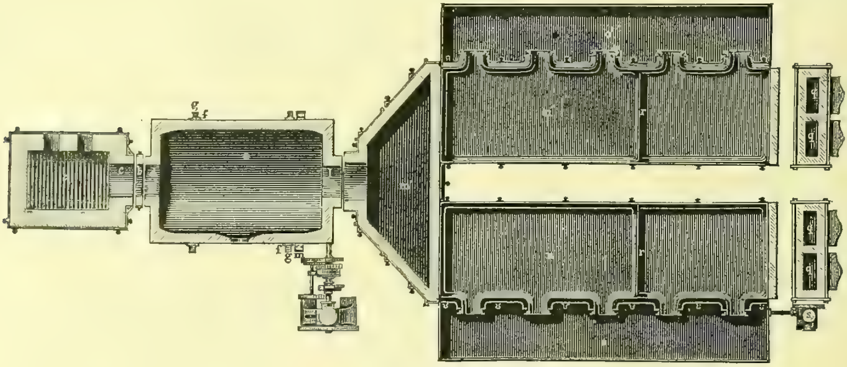

Fig. 34.

Revolving black ash furnaces. Anybody who considers the kind of work done by a ball-furnace man will come to the conclusion that this work can be done more efficiently and cheaply by mechanical means, as it simply consists in keeping the charge turned over. The actual solution of this problem proved, however, a difficult task, even after the right principle, that of a cylindrical furnace revolving as a whole, had been found by Elliott and Russell, in 1853. Apart from the mechanical imperfections of their furnace, it turned out the black ash much too hard and in a very bad state for dissolving, just because by the continuous rotation all the gas was driven out, and the honeycombed structure of the balls was lost. Stevenson and Williamson, in 1855, overcame both difficulties, and must be called the true originators of mechanical blackash furnaces, which have now superseded hand-wrought furnaces at most of the larger British and at some of the Continental alkali works.

Figs. 34 and 35 show an ordinary revolving black ash furnace in sectional plan and in elevation. *a* is the fireplace, with two working doors and a cylindrical opening, $2\frac{3}{4}$ feet wide, for the flame to pass through. Between this and the revolving cylinder there is a fire-brick lined, cast-iron ring *b*, the 'eye,' hung by means of chain and pulleys, which allows some air to enter all round, and the necessary expansion to take place. The cylinder *e*, consists of a shell of $\frac{1}{2}$-inch boiler plates, $15\frac{1}{2}$ feet long and $10\frac{1}{4}$ feet wide inside; cast-iron tire seats *ff*, and cast-steel tires *g g*, shrunk upon the barrel, work upon the V-rollers *h h*. The cylinder is lined inside with fire bricks, 9 inches thick in the centre, $1\frac{1}{2}$ feet at the ends; this facilitates the running out of the charge. Two horizontal 'breakers' project from 9 to 13 inches above the other lining, and promote the mixing of the charge in revolving. A $1\frac{1}{2}$-foot manhole, closed by an iron lid, allows charging and emptying the furnace. Each furnace is provided with a special engine, possessing double gearing so that it can produce either a slow movement (one revolution in four minutes) or a quick movement (five revolutions per minute). The highest velocity practically employed is one revolution per minute. The gearing acts upon a spur-wheel *m*, made in one piece and bolted immovably to the furnace. The exit opening *l* communicates with the large dust chamber *m'*, to which are joined the two boiling-down pans *n* and *n'*, 28 feet long by 8 feet wide by $2\frac{1}{4}$ feet deep each, with their drainers *o* and *o'*, and from these the flame goes through the flues *q q* into a special chimney, 6 feet wide and 100 feet high. The partition *r* in the pans has the object of reserving one part for evaporating the mother-liquor pumped up from the drainers.

A railway runs above the furnaces for charging them, and another (smaller) railway runs underneath them for moving the discharging 'pots,' each of which yields a ball of about the same size as those made by hand. A mechanical furnace must have a number of pots corresponding to its size.

A furnace of this size takes charges of 30 cwt. saltcake and gets through 15 to 18 tons of saltcake in twenty-four hours, with a consumption of 13 cwt. of coals per ton of saltcake. Much larger furnaces have been erected, *e.g.* some at St. Rollox, where the shell itself is barrel-shaped, $18\frac{1}{2}$ feet long, $12\frac{1}{2}$ feet wide in the centre, $8\frac{1}{2}$ feet wide at the ends. This furnace works 4 tons of saltcake every two hours, or 50 tons in twenty-four hours. A furnace erected by the Widnes Alkali Company in 1887 (described by Watson Smith in S. C. I. 1887, 417) is cylindrical, 30 feet long, $12\frac{1}{2}$ feet wide, with three doors. Each charge contains 8 tons 12 cwt. saltcake, along with the requisite calcium carbonate and coal. In a week of seven days it makes 48 charges, containing 400 tons of saltcake, and yields 240 tons of 60 p.c. caustic. This furnace takes only 10 cwt. of coals to a ton of saltcake.

Revolving ball furnaces are mostly heated by means of very large ordinary fire-grates. Gaseous fuel, it is stated, has not been found suitable in this case; but it is difficult to reconcile this with the all but universal preference given to gas producers in nearly every other kind of operation where a high heat is required.

The usual way of working revolving furnaces is to introduce first all the chalk or limestone (lime-mud, &c.) with two-thirds of the coal, and to keep this slowly moving round till the appearance of a blue flame of CO round the man-hole shows that some caustic lime has been formed. This 'liming' lasts about 1 to $1\frac{1}{2}$ hours. Now the saltcake, together with the remainder of the coal, is put in, and the rotation is slowly continued for some time, till the mass is nearly fused, when the quick movement is started, and is continued till bright-yellow flames break forth from the pasty mass within the furnace. The furnace is turned round very quickly several times, so as to detach the mass from its sides; the man-hole is knocked off, and the cylinder is turned out to discharge its contents into the row of pots, which are pulled away as they are one after another being filled.

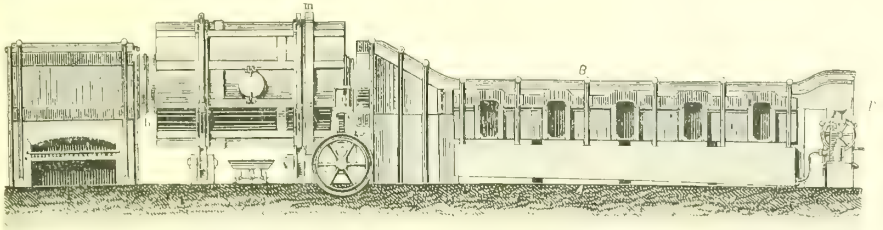

Fig. 35.

The object of 'liming' is to produce a certain proportion of caustic lime, larger than with hand-wrought furnaces, which in the lixiviating tank will cause the balls to burst, and to be more easily dissolved. Without this, as they are not sufficiently porous, there is very much loss, both by incomplete exhaustion and by the necessary elevation of temperature which produces Na_2S. But the 'liming' greatly prolongs the operation, and hence many attempts have been made to supersede it by other means. The most notable is that of Mactear (patented in 1874). He charges saltcake, coal, and limestone all at once. Of the latter he takes only the theoretical quantity, but when the decomposition has been achieved, he stops the revolver and throws in 10 per cent. quicklime of the weight of the saltcake, with 15 per cent. furnace cinders, both in order to achieve the same end as by 'liming.' The ash made by this process is not quite so strong as by 'liming,' and it seems certain that more limestone than the quantity prescribed by Mactear must be used.

Péchiney (patents of 1877 and 1878) adds at the end of the operation some saltcake, which has the effect of destroying the cyanide present (perhaps by the reaction: $2NaNC + Na_2SO_4 = Na_2S + Na_2CO_3 + CO + 2N$), and of preventing the formation of ferro-cyanide, which further on, when being calcined, imparts a yellow tinge to the soda ash. Weldon adds with the saltcake some limestone dust, which decomposes the Na_2S present and yields better tank liquors. This is all the more necessary as the Na_2SO_4, in destroying the cyanide, is reduced to Na_2S. The Péchiney-Weldon process seems to be the best of those proposed; but even this process does not seem to be very much practised now; usually all the materials are charged at the same time, and, with a proper mixture, good black ash is obtained without further difficulties.

According to Jurisch (see below), the analyses of black ash and tank liquor, produced by various systems of working, prove that the quantity of cyanides depends simply upon that of the undecomposed sulphate, and it is indifferent whether this be present all along or is only added at the finish. The advantage of the Péchiney-Weldon process seems to consist chiefly in the fact that a product is obtained containing always the same known quantity of sulphate sufficient to keep down the cyanides nearly to the point of hand-made black ash—a result which cannot be quite so easily attained by discharging the revolver rather sooner.

Several other patents were taken out about the same time (1878) for destroying the cyanide and ferrocyanide, by Mactear, Gaskell, Deacon & Co., Pauli, Brunner, Allhusen, and Glover, but these have hardly come into extensive use.

Probably the most successful plan is that of deferring that destruction till after lixiviation, as we shall see below.

T. W. Stuart (S. C. I. 1884, 607) sums up the relative merits of revolvers and hand furnaces as follows. Revolvers cost considerably more than hand furnaces for a given quantity of work; there is no saving of coal or limestone, and the colour of the finished soda-ash [probably owing to a larger production of ferrocyanide] is not so good as that produced from hand-made balls. Labour in revolvers is only 1*s.* per ton on sulphate, as against 3*s.* in hand furnaces, but of this saving of 2*s.* per ton 1*s.* must be deducted for the increased cost of repairs and stores. But there are indirect advantages in favour of mechanical furnaces: better decomposition of the sulphate, stronger ash, better yield, dispensing with a large number of troublesome men, easy control of the operation of balling, regular and certain results. In large works nobody would like to go back to hand furnaces, but the direct saving by revolvers is not large enough to justify their erection in small works.

Properties of black ash. The yield of black ash is about $1\frac{3}{4}$ times the weight of the salt cake furnaced. Properly made, black ash has a blackish-brown, in some places a liver-brown, surface; on breaking, it exhibits a slate-grey colour and porous, almost pumice-like, structure, and looks homogeneous all over, without any black or white streaks or lumps. Balls which are quite black on the outside are made with too much coal, or are very badly wrought, so that the mixing coal was not all consumed and the ball could not be 'cleared.' If there was a deficiency of limestone, or if the balls were overheated, they are very dense, with pale pink spots outside, and on breaking their colour is pink or purple, in the worst case brick-red. Such black ash contains very much sodium sulphide or even polysulphide. Kolb found this to occur whenever the melting-point of silver was exceeded. 'Soft' balls occur when the temperature has not been high enough, so that the mass never got beyond the thinner state to the pasty, porous one. Such black ash is very difficult to lixiviate, and contains much undecomposed sulphate. The black ash from revolving furnaces is always much denser than that from hand furnaces.

In order to check the furnace men, samples are taken from each man's work, sometimes even from every single ball, and are roughly tested for their percentage of alkali, of sulphate, and of sulphide; but as these cannot be average samples, the judgment of a practised eye on the appearance of the ball in general must always be taken into account as well. The testing-methods are the same as those used for tank-liquor (see below).

Of the published analyses of black ash many are not trustworthy, because they were evidently made with a material changed by exposure to air, or because they neglect constituents which must have been present; some of them also because they give highly detailed figures for constituents for which no good analytical methods are (or were then) known. We quote only a few:—

—	From Liverpool (Kynaston)	From Jarrow (Stohmann)		From Amiens (Kolb)
		Hand made	Revolver ash	
	a	*b*	*c*	*d*
Sodium carbonate	36·88	44·41	43·27	44·79
„ silicate	1·18	—	—	1·52
„ aluminate	0·69	—	—	1·44
„ sulphate	0·39	1·54	1·06	0·92
„ chloride	2·53	1·42	1·48	1·85
Calcium oxide	9·27	10·44	7·13	9·68
„ sulphide	28·68	28·87	27·73	29·96
„ carbonate	3·31	3·20	7·52	5·92
„ sulphite, &c.	3·78	—	—	—
Magnesium oxide	0·25	0·10	0·19	—
Silica	—	0·89	1·74	—
Ferric oxide	2·66	1·75	1·48	1·21
Alumina	1·13	0·79	0·72	—
Iron sulphate	0·37	—	—	—
Ultramarine	0·96	—	—	—
Sand	0·90	2·20	2·66	—
Coal	7·01	5·32	5·28	1·20
Water	0·22	—	—	—
Total	100·21	100·93	100·26	98·49

These analyses do not show caustic soda, which is, in fact, only formed on lixiviation; neither do they count up a number of rare substances, found by some authors in the samples examined by them. But the analysts ought not to have neglected the cyanide, nor the soda present in an insoluble form. There is also no mention of Na_2S, which is never quite absent. All these are accounted for in the following partial analyses of black ash made by the Péchiney-Weldon process :—

—	Made with 60 per cent. coal on the sulphate	100 sulphate, 77·8 limestone, 36·1 coal	100 sulphate, 85·3 limestone, 44·1 coal
Alkali	22·60—24·51	24·25—26·00	23·00—26·25
Na_2S	0·28— 0·38	0·31— 0·48	0·20— 0·37
Na_2S to 100 alkali . . .	1·15— 1·60	—	—
Na_2SO_4	0·41— 0·63	0·18— 0·90	0·18— 0·90
Total Na_2SO_4 after oxidation .	1·85— 2·24	0·88— 1·90	0·96— 2·00
Available alkali in soda ash .	57·40—58·30	—	—
Alkali in soda waste . . .	0·21— 0·37	0·19— 0·23	0·17— 0·32
Na_4FeCy_6	—	traces— 0·06	traces— 0·052

Jurisch (S. C. I. 1880, p. 241) gives the following analyses (in which we abridge the three decimals of the percentages to one):—

—		Musspratt, revolver, July 1874	Muspratt, hand, November 1874	St. Rollox, Mactear's revolver process, February 1886	Muspratt, Mactear's revolver process, April 1886
Mixture :	Salt cake . .	100	100	100	100
	Limestone . .	106	109	73	78
	Coal 10 p.c. ash .	55	56	41	47½
	Mactear's lime .	—	—	7	7½
Na_2CO_3		41·6	41·8	45·3	46·2
NaCl		1·2	1·4	1·7	0·7
Na_2SO_4		1·2	2·3	1·5	0·4
Na_2SO_3		0·14	0·5	—	—
$Na_2S_2O_3$		—	0·3	1·3	0·6
SiO_2		2·4	4·1	3·1	2·7
Al_2O_3		1·1	1·5	1·0	0·8
Fe_2O_3		0·9	1·1	0·7	1·0
$CaCO_3$		11·6	6·6	5·1	9·7
CaO		5·7	5·8	1·3	1·7
CaS		29·8	31·9	31·0	33·6
MgO		—	0·3	0·3	0·4
Coke		4·4	3·3	7·4	3·5

Black ash keeps unchanged in the absence of moisture and CO_2, but in the presence of these it soon undergoes a change (minutely studied by Kolb, A. Ch. [4] 7, 118; 8, 135; 10, 106). The lime attracts both H_2O and CO_2; on being hydrated it swells up and cracks the balls, which gradually fall to powder. On lixiviating, they now yield less NaOH, but, on the other hand, much more Na_2S and products of its oxidation, since the action of the atmosphere on CaS produces calcium hydrosulphide, polysulphide, thiosulphate, and other soluble calcium compounds which, on lixiviation, at once react on sodium carbonate and destroy part of this. In the course of time the reaction may thus be reversed, and the sodium carbonate may be entirely decomposed again. Hence black ash ought not to be kept too long before working it up, and ought not to be exposed to the action of the air after being once cooled down.

The action of *water* on black ash has also been studied minutely by Kolb (*l.c.*). From his experiments he draws the following conclusions. The quantity of NaOH formed in the digestors, by the action of lime on sodium carbonate, is not materially influenced by the quantity of water, but increases both with the time of digestion and the rise of temperature. Almost exactly the same conditions govern the formation of sodium sulphide, but this is independent of that of caustic, and evidently takes place by the action of dissolved CaS on Na_2CO_3. NaCl slightly increases, Na_2SO_4 slightly diminishes, the quantity of CaS entering in solution, which always takes place in the shape of $Ca(SH)_2$. Boiling CaS with water will effect this slowly. Solutions of Na_2CO_3 act all the more on CaS the more dilute and the hotter they are, and the longer they remain in contact with each other; the presence of caustic lime or caustic soda retards this action. Hence the lixiviation should be carried on as quickly and at as low a temperature, and with as little water, as possible.

A special treatment of black ash has been proposed by Mathieson and Hawliczek (Germ. Pat. 5,456, 1886) in order to purify it from cyanide and sulphide. They expose it in closed vessels to superheated steam at a temperature of 300°–500°C., whereby the cyanides are decomposed, with formation of ammonia, which may be recovered and utilised. By then exposing the mass to a temperature of 550°–650°C. the sulphides are decomposed, with evolution of sulphuretted hydrogen. (Experience must show whether this process acts completely and is sufficiently cheap.)

Lixiviation of Black Ash.

During the first period of the manufacture of artificial soda, the black ash, as it came out of the furnace, was directly sent out to soap makers and other consumers. This is now done only quite exceptionally. Usually (in England universally) the black ash is separated by *lixiviation* into a soluble and an insoluble portion. The former yields commercial soda ash, crystals or caustic; the latter, which contains CaS, as well as many impurities, is a waste product, until quite recently very imperfectly, if at all, utilised.

The lixiviation is not merely a mechanical process for dissolving the soluble matter; during its course chemical reactions set in, which are partly comparatively harmless (as the formation of some NaOH), but which may cause very much loss by the conversion of Na_2CO_3 into Na_2S, Na_2SO_4, and intermediate states of oxidation, as will be understood from the remarks made upon the action of water on black ash.

Properly made, porous black ash requires only breaking up into large pieces, so that it can be handled; but dense, overheated or underheated black ash must be crushed to a coarse powder, and even then is nothing like completely exhausted, without reconverting much of it to Na_2S. It is, of course, the first requirement that black ash should be completely exhausted, that the liquor should be pure, and that it should be as concentrated as possible. We have seen above that this can be done only by working quickly and at a moderate temperature. The latter is specially required for weak liquor, which is much more liable to act upon CaS than concentrated liquor. The former should never be hotter than 43°C., and is much better kept between 32° and 37°C.; the latter may get up to 60°C.

It is further necessary to disturb the solid mass as little as possible, in order to prevent the liquor from becoming muddy; and, more particularly, any exposure of the wet solid residue to the atmosphere must be avoided, because this leads to a rapid oxidation of CaS, even as far as $CaSO_4$, and a consequent loss of soda.

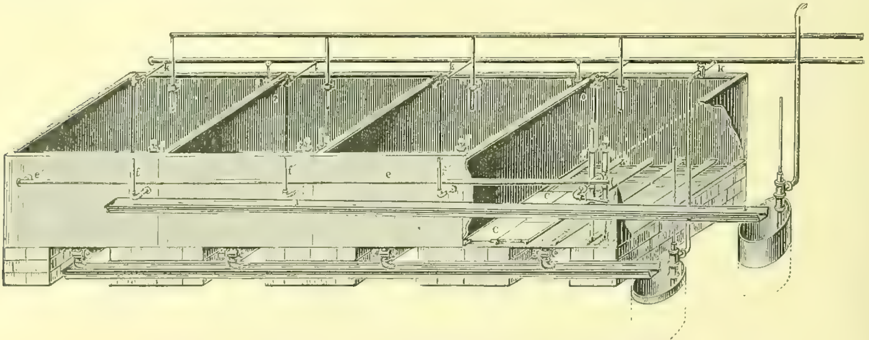

FIG. 36.

The different apparatus formerly employed for lixiviating soda ash need not be described here, as they are completely obsolete now. The apparatus universally employed now was originally invented by Professor Buff, of Giessen, but was apparently first employed in practice by Dunlop, at St. Rollox, in 1843, and made its way very slowly, first into Lancashire (about 1860); in England it seems to have been dominant about 1864, on the Continent ten years later. Its principle is: allowing the black ash to remain in the same place, and causing the liquor to circulate in a methodical manner, so that it is brought up to concentration, and the black ash is completely exhausted at the same time, without ever being exposed to the air. By this course the liquors are much stronger and purer, and the process is much less expensive than with the plans formerly practised.

The way of carrying out the above principles is shown in fig. 36. A number of 'tanks' or 'vats'—at least four, but sometimes five, six, or even more—is combined to form a set. The tanks must be all on the same level, and this should be so far removed from the ground, by means of pillars, that no leaks can occur without being observed. They are made of cast iron, or, preferably, of wrought iron. Near the bottom there is a row of T-pieces *bb*, for supporting the perforated plates *cc*, forming a false bottom. Whilst the true bottom is often made to slope to one side, where the outlet cock is placed, the false bottom must be quite horizontal. Each of the tanks contains two overflow pipes, one, marked *e*, for weak liquor, and another, marked *f*, for strong liquor. This is best seen on the section, fig. 37. They are cast-iron pipes, a little wider in the upper part, with a conical plug fitting into a seat bored out at the enlargement. Above the plug-seat the pipe has a side-branch, bolted to one side of the tank, where there is a corresponding hole. The pipes pass through the false bottom, and the liquor can enter into them from below. If the plug is taken out, the liquor contained in the corresponding tank will rise from its bottom in the pipe *e* and will overflow into the next tank near its top, and thus a continuous stream of liquor may be produced right through the whole set of tanks. Where, however, it is intended not to run the liquor upon the next tank, because it is concentrated enough to be run off, the pipe *e* will be kept closed and the plug taken out of pipe *f*. All the pipes *f f* are arranged on the front side of the set; they are, on the outside, provided with swivel-pipes *f'*, which, when turned up, prevent the liquor from running out. By turning the branches *f'* downwards at the same time as the plugs are taken out, the strong liquor runs into the shoot *i*, and from this into the well, from which it is pumped into the settlers.

At some works there are cocks instead of the swivel-pipes *f'*; at others the strong liquor pipes *f f* are omitted, and the strong liquor is run off by means of the bottom-cocks *g g*, which must be provided in any case; but neither of these plans can be recommended. The bottom cocks *g g* serve for running away the weak liquor previously to casting out the solid waste. This liquor passes on to a separate well, from which it may be pumped into the water-conduit *k*, from which the tanks are supplied by a separate branch each. A special set of pipes serves for supplying either steam or hot water, as the case may be.

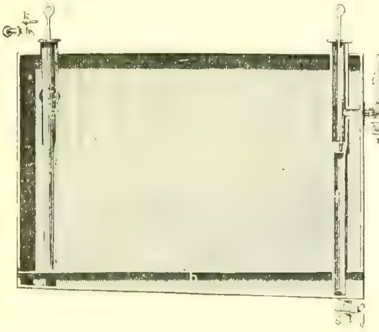

FIG. 37.

The *working of the tanks* is carried on as follows: supposing a tank A has been exhausted. It is now filled with the solid residue, 'tank waste,' and with a very weak liquor, standing at about 1°Tw., and containing, together with some carbonate and caustic, also a considerable proportion of Na_2S. If it is run away, it causes not merely loss, but also nuisance, and it should therefore be used over again in lixiviation; the Na_2S will, later on, be removed by the carbonating process. In any case, this weak liquor must be run out of the tank by the cock *g*, whereupon the waste is 'cast,' unless the tanks are constructed for treating the waste at once by Mond's sulphur-recovery process. The empty tank should now be thoroughly cleaned and washed out, taking out the false bottom, so that the space underneath can be equally freed from liquor and mud. The false bottom is now replaced, and is first covered with a 3-inch layer of furnace-cinders, freed from dust and ashes by riddling. The remaining space of the tank is now filled with black ash, using the smaller lumps and the powder for filling up the interstices between the large lumps. It is now ready to be connected with the preceding tank B, which in the meantime had been furnishing strong liquor, but which must have gradually gone down in concentration. When the hydrometer shows, say, 42°Tw. (some stop at 46°Tw.) the pipe *f* in tank B is closed and the pipe *e* is opened, so that the liquor rising up from the bottom of B flows over into A, and 'covers' the freshly put in black ash. This should be done completely; any projecting pieces must be pulled down with a hook, as the action of the air is most injurious in the moist state (see above). There will be a considerable rise of temperature in A, especially if the black ash had been put in warm, which is preferable; but, apart from this, the hydration of the anhydrous salts, and the chemical reaction between $Ca(OH)_2$ and Na_2CO_3 are all accompanied by evolution of heat. So long as this does not exceed 60°C. it is harmless, and is even conducive to better lixiviation.

The concentration of the liquor, of course, rises at the same time, and this may be promoted by allowing it to stand some time on the fresh black ash before running it off; but if allowed to get beyond 57°Tw. it is liable to be contaminated by Na_2S, and especially by the double compound of FeS and NaS, which imparts a dark yellow or green colour to it. This liquor is run into 'settlers,' and should be tested at least once a day. The testing methods will be described below.

We shall now look at the other end of the series, for it is evident that the flow of liquor from B into A must be produced by weaker liquor flowing from the bottom of C on to the top of B, and still weaker liquor from the bottom of the last tank D on to the top of C, the whole being started by fresh water running on to the top of D. (During the time that one of the tanks is being 'cast' and refilled there is, of course, only a set of three working at the same time.) The water (mixed, as before stated, with some of the waste liquor from a previous operation) is sometimes, in summer weather, employed at the ordinary temperature; more usually it is employed in a tepid state, but even in winter it ought not to be warmer than 37°C. The colder the water in the weak tank is kept the purer the liquor will be, and the necessary temperature is best imparted by injection of steam just under the surface in the intermediate and the strong tank.

The points to be attended to in lixiviation are, first, the proper temperature of the water running in and the liquor running out. Second, the strength of the latter and its chemical composition—that is, its deterioration in the process. Third, the proper exhaustion of the black ash, so that the tank waste does not contain more than a minimum of available soda in the soluble state. The *insoluble* soda, which may cause a considerable loss, is not affected by the way the lixiviation is conducted, but by the mixture of raw materials for the black ash process, by the quality of the mixing coal, &c.; it can, however, only here be tested for.

Testing methods for black ash, tank liquor, and tank waste. In order to test *black ash*, a sample consisting of several pieces of the ball (which unfortunately can never be a real average sample) is finely powdered, and 50 grms. of it are digested with tepid water, free from oxygen and carbonic acid; the solution is made up to 500 c.c., and is now tested just like the tank liquor obtained on the large scale. Sometimes, previously to this, the muddy liquor is tested without subsidence for free and total lime; usually only the clear liquor is tested as follows:

1st, for *total available alkali*, by means of standard hydrochloric acid and methyl orange; 2nd, for *caustic*, by addition of barium chloride and titrating with hydrochloric or oxalic acid (in the last case without filtration); 3rd, for *sulphide*, by means of iodine; 4th, for *sulphate*, by means of barium chloride, either gravimetrically or volumetrically (the latter process saves hardly any time in this case); 5th, for *total sulphur*, by oxidising with bleaching powder and estimating the sulphate formed; 6th, for *chloride*, by standard solution of silver nitrate, after having exactly neutralised the alkali by nitric acid and boiled away the H_2S; 7th, for *ferrocyanide*, by means of Hurter's copper sulphate solution. *Tank waste* is mostly only tested for *available soda* by treating a solution, obtained as previously described in the case of black ash, with CO_2, boiling, filtering, and titrating the clear portion; sometimes also for *total soda*, including the *insoluble* portion, which is a somewhat lengthy process. (Details of all these methods in Lunge and Hurter's Alkalimakers' Handbook, 2nd edit., p. 128 *et seq.*)

The following analyses by Jurisch (Chem. Ind. 1880, p. 441) show the composition of revolver tank liquors (abridging the useless three decimals to one):—

—	Average of four months		Highest figure		Lowest figure	
	Grms. per litre	On 100 parts available soda	Grms. per litre	On 100 parts available soda	Grms. per litre	On 100 parts available soda
Total Na_2O . .	188·0	—	198·4	—	168·9	—
Na_2O as Na_2CO_3 .	147·9	—	161·2	—	131·7	—
Na_2O as NaOH .	40·0	21·3	47·7	24·8	37·2	18·7
Na_2CO_3	252·9	—	275·6	—	225·2	—
NaOH	51·7	--	61·6	—	48·0	—
NaCl	10·7	5·7	15·5	8·1	6·3	3·2
Na_2SO_4	2·8	1·4	3·8	1·9	1·9	1·0
Na_2SO_3	0·3	0·1	0·5	2·8	0·1	0·1
$Na_2S_2O_3$ . .	1·3	0·7	2·1	1·0	1·0	0·5
Na_2S	4·1	2·2	5·0	2·7	2·9	1·6
Total Na_2SO_4 calcul.	13·1	7·0	14·7	8·0	10·7	5·7
Total Na_2SO_4 found	13·1	7·0	15·5	8·3	10·5	5·6
Na_4FeCy_6 . .	0·8	0·4	1·1	0·6	0·5	0·3
SiO_2, Al_2O_3, Fe_2O_3 .	4·7	2·4	5·6	3·0	3·8	2·1

A comparison between different systems of working is afforded by the following figures, stating grms. for each 100 grms. of available soda (as Na_2CO_3+NaOH) in tank liquor:—

—	Muspratt hand furnaces, 16 days' average	Muspratt revolvers, 30 days' average	Runcorn Soap and Alkali Works					
			Péchiney revolver			Péchiney-Weldon		
			average	highest	lowest	average	highest	lowest
Na_2O as NaOH . .	33·6	21·3	13·3	15·2	8·5	19·1	21·5	15·2
NaCl	7·3	5·9	—	—	—	—	—	—
Na_2SO_4	6·0	1·7	4·1	5·4	2·8	3·6	4·5	3·2
Na_2SO_3	0·4	0·2	—	—	—	—	—	--
$Na_2S_2O_3$ . . .	1·1	0·7	1·5	1·6	1·2	1·0	1·3	0·9
Na_2S	1·4	2·1	1·4	1·8	0·9	2·2	3·0	1·9
Total Na_2SO_4 cal. . .	10·9	6·8	9·5	10·6	7·8	9·4	10·8	8·0
Total Na_2SO_4 found . .	10·9	6·8	9·3	10·4	9·0	9·4	10·8	0·6
Na_4FeCy_6	0·1	0·4	0·2	0·4	0·2	0·2	0·3	0·2
SiO_2, Al_2O_{31}, Fe_2O_3 . .	2·7	2·4	—	—	—	—	—	—
Mixing proportions:								
Saltcake 96 p.c. . .	100	100	87·8	—	—	—	100	—
Limestone . . .	102·1	76	64·4	—	—	—	74·4	—
Coal	52·1	38	34·8	—	—	—	41·9	—
Mactear lime . .	—	8·3	—	—	—	—	—	—
Péchiney saltcake. .	—	—	12·2	—	—	—	11·6	—
„ limestone dust	—	—	7·3	—	—	—	7·0	—
Sifted cinders . .	—	10	—	—	—	—	—	—

The tank liquor is always too muddy for immediate further treatment, and must be *settled* first. This will cause the tank waste mechanically carried away to subside; at the same time the action of the air, or of the fire-gases, if such are passed over the settlers, will cause some of the ferro-sodium sulphide to be decomposed, and the FeS to be deposited along with alumina and silica, partly or entirely in the state of chemical combination. This is a preparatory action to the carbonating process proper.

The settling tanks should be protected from cooling down, otherwise much of the soda would crystallise out in an impure state; for this purpose, and for a partial evaporation and carbonation, they are sometimes arched over, and the waste fire-gases of some furnaces are passed through. They must be either in pairs, to be alternately filled and emptied, or, preferably, they are arranged lengthways, say for a length of 100 feet, so that the liquor continuously flows through the whole series, but in so slow a stream that the suspended matters have full time to settle down, and the liquor issues at the other end in a perfectly clear state.

The clarified tank liquor is sometimes run at once into the boiling-down pans, leaving any further purification to the 'carbonating furnace.' But this is decidedly irrational; the iron, the sulphide, and if possible the ferrocyanide, ought to be removed beforehand.

The iron in tank liquors is principally in the state of FeS chemically combined with Na_2S. Sodium sulphide dissolves not merely ferric oxide, but also metallic iron (Scheurer-Kestner, Bl. 36, 48).

The ferro-sodium sulphides, compounds of Na_2S with FeS in various proportions, have been investigated by several authors, especially Kolb (A. Ch. [4] 10, 106). They are black, and remain suspended, or perhaps dissolved, in solutions of sodium hydrate or carbonate, which are thereby coloured from green to brown, according to concentration. Their solubility increases with the concentration and the heat of the liquors; it is lessened by the presence of NaCl or Na_2SO_4, and formerly this was sometimes turned to practical account. The only thorough remedy is, however, found in destroying the Na_2S, which keeps the FeS in solution. Many proposals have been made for this object; but most of these are more specially adapted for purifying liquors intended for the manufacture of caustic soda, and will be described in connection with the latter. Such liquors as are intended for the manufacture of soda ash are generally purified by *carbonating*—that is, treating them with CO_2 till the sodium hydrate and sulphide are both converted into Na_2CO_3, when the FeS will be precipitated, and can be removed by mechanical means. This process seems to have been first employed by Boeringer in 1838.

Carbonating tank liquors has the further effect of precipitating the silica and alumina, present in the shape of sodium silicate and aluminate. It has been observed by various chemists that in this case distinct chemical compounds of alumina and silica, sometimes double silicates of sodium and aluminum, are formed. It has even been noticed that the addition of alumina in the shape of bauxite removes the silica more completely (Eng. Pat. 1,161, 1881, of Carey, Gaskell, and Hurter). There is also some separation of a sodium-calcium carbonate $Na_2CO_3,CaCO_3$ 5aq, identical with the mineral gay-lussite (Reidemeister and Rammelsberg, Monatsber. d. Akad. d. Wissensch. Berlin, 1880, p. 783), and of a silico-carbonate of sodium, calcium, and aluminium: $Na_{18}Ca_4Al_2(Si,C)_{21}O_{63}+30aq$. Stroof (W. J. 1872, p. 259) and Wright (C. N. 16, 17) have found aluminium-sodium silicates, Scheurer-Kestner (Rép. Chem. appl. 3, 446) an aluminium silicate, and Petersen (Ber. 5, 409) normal sodium silicate, Na_2SiO_3, 5aq.

The carbonic acid for this purpose is, of course, rarely employed in the pure state, as it is obtained by means of limestone and hydrochloric acid. Usually lime-kiln gases, drawn off by a pump, or even by a chimney, are employed; sometimes waste fire-gases are used, but as these always contain oxygen the action is more complicated and there is more loss of soda, since some of it is not converted into carbonate, but into thiosulphate, and further on into sulphate. The most convenient and at the same time the cleanest way is to add a solution of sodium bicarbonate till all NaOH and Na_2S are converted into Na_2CO_3. Formerly this process was too expensive, but at present it might probably pay in some places. It should, however, be noticed that the reaction $2NaHCO_3+Na_2S=2Na_2CO_3+H_2S$ is not completed instantaneously, but requires some time and the action of heat.

Lime-kiln gases generally contain 20–25, rarely as much as 30, p.c. CO_2 by volume, fire-gases rarely above 10 p.c., unless they come from gas-producers, when they may get up to 18 p.c., with only 3 p.c. of oxygen.

Where carbonic acid gas in a more or less pure state is employed, this can be done in two ways, either allowing the gas to act upon the tank liquor, spread upon a large surface by means of a tower or column filled with porous material, or forcing the gas through a column of liquor contained in a tank. The former plan requires less force, but is not quite so efficient, especially as far as the utilisation of the CO_2 is concerned, as the latter, unless the carbonating columns are made of a very large size. These columns are made of iron, usually in a circular form; they are best fitted with inverted flower-pots or other fragments of earthenware, since coke is easily choked with the deposit formed, and is not as easily cleaned again. It has been observed that this choking takes place to a very much smaller extent if the gaseous current is passed from the top downwards, in the same direction as the liquor flows.

A very efficient carbonating tower is made by suspending, within an otherwise empty iron tower, a large number of chains, or of wire ropes, weighted at the ends, along which the liquor is made to run down, thus presenting a large surface to the gas without much danger of choking up; this danger can be entirely prevented by now and then shaking the chains, or blowing steam through the tower.

Where it is preferred to force the carbonic acid through the liquor itself, it is preferable to employ two or three cylinders, about six feet high each, and work them so that the partially-spent gas passes through a freshly-charged cylinder, and the fresh gas through the nearly carbonated liquor.

The carbonated liquor must in any case be freed from the newly formed precipitate by another settling operation, altogether similar to the first, before being run into the concentrating pans.

At some works they submit all soda liquors to the process of *oxidation* (p. 471 and 480).

Removal of the ferrocyanide. Even carbonating the liquor is not sufficient to remove the iron completely, since some of it is present as sodium ferrocyanide, which, in the operation of calcining, produces ferric oxide, and thus stains the soda ash, in which the presence of about 0·003 p.c. of iron is quite perceptible. If the mixing contains very little nitrogen, or if the conditions of the black-ash process are such as to produce very little cyanide—*e.g.* by the Péchiney-Weldon process—the quantity of ferrocyanide formed is mostly so insignificant that it can be neglected. But usually that is not the case, and a process for freeing the liquors from this impurity should be very welcome. T. Williamson stated, in 1866, that it could be removed by heating the strong liquor in a steam boiler to 155°C., when the salt is destroyed and the iron separated in an insoluble form; but the formation of hard crusts at the sides of the boiler was an inseparable drawback to his process, nor is the decomposition of the cyanide complete at that temperature.

Since the year 1878 the removal of the ferrocyanide again attracted great attention. It became much more urgent than before, because, on one side, the tendency to the formation of cyanides is much greater in revolvers than in hand-furnaces (owing to the better decomposition of the sulphate), and because, on the other hand, the consumers had become accustomed to the very white colour of ammonia ash. This led to a renewed attempt to purify the tank liquor itself, by the process of Carey, Gaskell, and Hurter (Eng. Pat. 2,939, 1879, and 5,310, 1882). It rests on the fact that the ferrocyanide is destroyed, in the presence of sodium thiosulphate, at a temperature of 180°C. (corresponding to a pressure of 10 atmospheres), probably by the following reaction:

$$\begin{aligned}&Na_4FeCy_6 + 6Na_2S_2O_3 + 2Na_2CO_3 + H_2O\\&= 6NaCyS + 6Na_2SO_3 + 2NaHCO_3 + FeO.\end{aligned}$$

If Na_2S is present, the FeO passes into FeS, which settles out after some time. During this process any alumina and silica present are precipitated in the form of crusts which quickly stop up the pipes; nor must the liquor be too concentrated, because then Na_2CO_3,H_2O is separated in hard crusts.

The process is carried out as follows. The tank liquor is thoroughly carbonated and oxidised by injecting into it waste fire-gases, aspirated from a revolver-chimney. This operation converts all the caustic soda into carbonate, produces a certain quantity of bicarbonate, and oxidises part or all of the sulphide to thiosulphate; it also precipitates all the alumina and part of the silica (nearly all if bauxite had been added on purpose, *cf.* above). The settled and filtered liquor is heated up to 100°C., and is then pumped through a superheater, consisting of a coil of wrought-iron tubing, 2 inches wide, of a total length of 1,200 feet, provided with a pressure gauge, indicating up to 40 atmospheres. This coil of pipes is heated in a furnace, the space inside the coil being filled up with a network of bricks, serving as a heat regulator. The pressure is kept up by a valve loaded to 15 or 20 atmospheres; the liquor must pass through from the top downwards. After passing through the superheater, the liquor must have another settling before being run into the boiling-down pans. Such a coil of pipes lasts a few months before being stopped up with sediment inside and burned outside. This process pays only for the manufacture of 'crystal carbonate' and similar pure products.

Newall and Sisson (S. C. I. 1887, 349), who make soda crystals direct from carbonated tank liquors, remove the ferrocyanide present in the mother-liquor by agitating them with a zinc salt and blowing in carbonic acid at the same time. Ferrocyanide of zinc is precipitated and separated by a filter press; it is decomposed by caustic soda, or by calcium sulphide. The resulting solution of sodium or calcium ferrocyanide is utilised for the production of Prussian blue, and the zinc oxide or sulphide is used over again.

None of the above-mentioned processes remove the sodium *sulphocyanide*, but this salt is harmless, being destroyed in calcining the soda ash without leaving any coloured residue.

According to Mathieson and Hawliczek (Germ. Pat. 40,987, of 1887), soda liquors can be purified both of cyanide and sulphide by treating black ash in closed vessels with overheated steam. At 300–500°C. the cyanide is decomposed, with evolution of ammonia, which can be recovered; at 550–650° the sulphide is decomposed as well, with evolution of H_2S.

The concentration of tank liquor (whether carbonated or not) always takes place in iron pans, heated by the waste fire of the black-ash furnaces. One kind of pan, that which is heated by fire playing on the top of the liquor, has been described above in connection with the black-ash furnace. These pans are usually (but not exclusively) employed for non-carbonated liquors; they work very economically, and require hardly any repairs, since the fire does not touch their bottom, and the crusts formed there are not excessively hard, but they have the drawback that the liquor is contaminated by flue-dust coming over from the black-ash furnace, especially also by particles of saltcake mechanically carried away, and that the sulphurous acid, never absent in coal fires, causes a not altogether unappreciable loss of soda. There is also some liquor carried away by the draught, in very small drops.

There ought to be another pan, either above the arch of the first, or elsewhere, heated by the still existing heat of the fire-gases leaving the principal pan, where the liquor is stored up for feeding the latter, and where it at the same time receives a final settling.

Before charging a pan, the flanges of the doors are covered with lime-putty; the doors are put on and screwed fast. Even if the joints should not be absolutely tight at first, they will soon become so, and any liquor oozing out is not lost, as it is caught in the drainer. The pan is now filled nearly to the top, and as the liquor evaporates, more is run in from the store-pan, till the pan is filled with a thick magma of salt and mother-liquor. Most of the salt forms near the firebridge, where the liquor boils most strongly, and the attendant must rake this away towards the back end of the furnace. At the end of the operation the screw bolts of the doors are loosened, the liquor is allowed to run out, and the pasty mass of crystals is raked out into the drainer.

Where carbonating is done by sawdust, this is mixed with the salt in the pans before pulling it out into the drainers.

The 'black salt' thus obtained is essentially monohydrated sodium carbonate, with more or less impurities, and more or less soaked with mother-liquor. Where the latter is not treated separately, but is always pumped back into the pan, it is not of very much importance to take it out of the black salt; but even then it will be best to drain the latter thoroughly, or even wash it in order to obtain very strong ash, and confine the boiling down of the mother-liquor to separate pans, or to a separate division of the same pan (*cf.* fig. 34). The draining can be greatly improved by employing either a vacuum or a hydro-extractor, and if necessary the same apparatus can be used for removing the last portions of mother-liquor by washing. In this way, with good sulphate, good black ash, careful lixiviation, and carbonated liquor, the greater part of the soda can be obtained as so-called 57 p.c. (in reality about 56 p.c.) alkali, along with some weak alkali (48 to 50 p.c.). Where the mother-liquors are converted into caustic, this is even easier to attain.

Another kind of evaporation by open fire is frequently carried out in France for obtaining *caustic soda ash.* There is a reverberatory furnace, covered by one or two pans, in which a first concentration of the liquor to 60 or 62°Tw. takes place, and from which the furnace is fed when ready for a new charge. The furnace-bed consists of fire-bricks or cast-iron plates, and is covered with a thick layer of dried soda salt. When empty this layer is levelled, and the furnace is made very hot; the liquor is then run in gradually, so that it evaporates almost as fast as it touches the bed, and a semi-fluid paste is produced, which is constantly turned over. The heating is continued at so low a temperature (about the fusing point of lead) that the mass, in spite of the caustic present, does not fuse, but is only dried. Such furnaces yield three or four batches of 6 cwt. or a little more each per twenty-four hours, with an expenditure of 80 parts of coal for 100 of soda ash. The latter comes up to about 50 p.c. of alkali, by the English test, with a proportion of about 1 Na_2O as NaOH to 4 of Na_2O as Na_2CO_3. This ash (*sels caustiques*) is in great demand by soap makers and bleachers.

Pans heated by bottom fire are regularly employed for concentrating caustic liquors, and very frequently also for carbonated tank liquors. They suffer more by the fire, require more labour, and turn out less work than 'open' pans; but they keep the liquor purer, and are more easily managed for separating the product into different qualities. They should be constructed in such a manner that the salt cannot collect on a surface touched by the fire, where hard crusts would be formed, and the pan would soon be out of repair. This is best attained by the 'boat-pans,' as shown in fig. 38, where they are represented as heated by separate fire-places (necessary for part of the pans for concentrating caustic liquor). These pans are made of cast iron, or, more usually, of wrought iron. The salt collects in the lowest part, which is not exposed to the fire, and is removed by 'fishing' it out with a perforated spade. Fresh liquor is run in from time to time, and the fishing is continued till the salts cease to be pure enough for best alkali. The mother-liquor is then either boiled down to dryness in a dished furnace, and yields weak ash, or, with uncarbonated liquors, caustic ash similar to that obtained in the French furnace (but more impure), or else it is worked up for 'cream caustic.'

It is possible by careful management of the fishing operation to obtain salts of different strengths, ranging from the purest down to very impure and strongly caustic ash, but it is hardly worth while doing so, since two strengths, the best and lowest, are quite sufficient, all medium strengths demanded being obtainable by mixing these two.

By very special care the monohydrated sodium carbonate, obtained in the evaporating pans can be obtained pure enough for direct use, as 'crystal carbonate.' We shall mention this in the section *Soda crystals.*

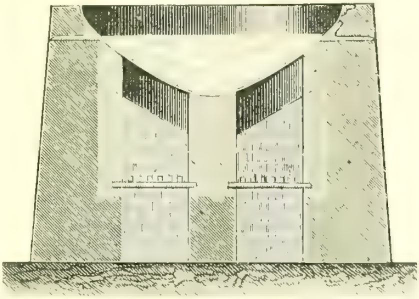

Fig. 38.

Mechanically-working pans have been constructed in great variety. One of the best of these is Thelen's fishing-pan, figs. 39 and 40. Upon the cast-iron semi-circular end plates the shaft W rests on two bearings. To this shaft the rods F are fixed, and are supported by stays; at their free ends they are provided with freely hanging, slanting scrapers G. These, on passing through the liquor, touch all the parts of the pan bottom, and move the salt towards the end, where it is scooped out by another shovel, and delivered over the side of the pan. Four pans require only one attendant, and ¼-horsepower each for the stirring apparatus; each pan, when fed with previously heated liquor, turns out 18 to 20 cwt. soda salt per 24 hours.

Attempts have been made, apparently first by Mr. John Dale, of Manchester, to *utilise the latent heat* of the vapours evolved in boiling down soda liquors, by making them work in a second pan, with the assistance of a vacuum. This principle, which had been known long before, and has led to a very great economy in the manufacture of sugar, seems to be less useful in concentrating soda liquors, and seems to have more drawbacks than advantages in this case, so that it has not met with much success. Contrary to the conditions of sugar-making, the quality of the product is not improved by the lowering of the temperatures produced by the vacuum. The salt adheres very strongly to the pans, which cannot be as easily cleaned as open ones; and the advantage is not so very great here, as there is generally enough heat to spare from the black-ash furnaces to do the concentrating work for nothing. Only in the case of caustic liquors this principle could be thought of, and here the action of the liquor on the pans is a drawback of some consequence.

Concentrating soda (and caustic) liquors in a vacuum has been patented by Buffet (Eng. Pat. 1,587, 1881). The apparatus consists of four vessels working in a set like those used of old for concentrating sugar liquor. The vacuum is made so strong that the evaporation takes place at 50°C. When the concentration has reached 36° Baumé, the carbonate liquor is run off to crystallisation. Caustic liquor is concentrated to 33°Baumé, and then conveyed into specially constructed evaporating vessels, where the carbonate salting out can be collected and removed from time to time.

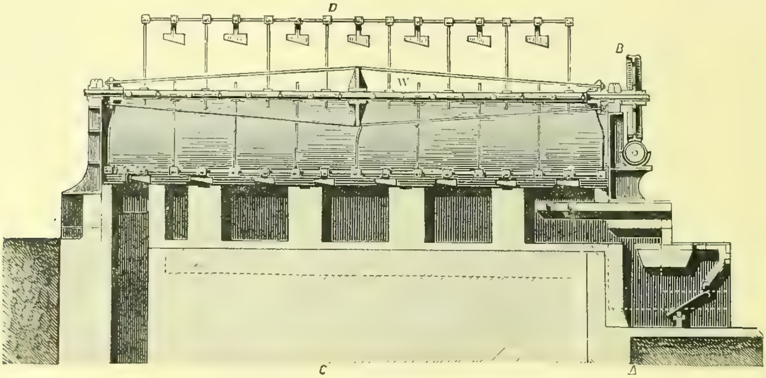

Fig. 39.

Finishing the soda ash. The 'black salt' must be freed from the last molecule of water it contains, and from any adhering organic impurities, by a calcining operation which in some cases is combined with a carbonating action. Where the liquor has been carbonated, the salt merely requires drying at a moderate heat, and ultimately bringing up to a red heat, but no fluxing need be apprehended, and the operation, which is always carried out in an ordinary reverberatory furnace, called 'finishing furnace,' is very simple.

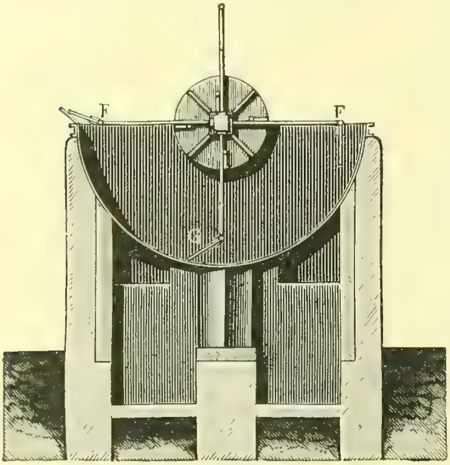

Fig. 40.

Non-carbonated salts, roughly mixed with sawdust as they are made on the Tyne, require much more care and experience. The operation of finishing is here called 'carbonating,' because the caustic soda, as well as the sulphide, must be converted into carbonate in the furnace itself, by means of the carbonic acid yielded by the burning sawdust.

The furnaces are double-bedded, and hold from 15 to 17 cwt. of soda ash on each bed; it takes about 5 or 5½ hours to finish a batch, so that one carbonating furnace suffices only for one ordinary ball furnace. The salt is first dried at a very low heat, and the fire is then raised very gradually, so that the caustic and sulphide do not fuse, which would impede the action of the air. The latter is needed for burning the charred sawdust, and must be promoted by constantly turning over the mass, so that at last all charcoal is burnt away and the mass is 'cleaned.' If this is done too quickly, the CO_2 formed goes away without carbonating the NaOH and Na_2S. Unless there is a great excess of air present, there will be even a fresh formation of Na_2S from Na_2SO_4. At last the mass is brought to a higher heat, but, if it is more caustic than usual, it does not stand this without softening. Only then the ferrocyanide is destroyed, and the carbon now produced can hardly be entirely burnt off. The ferric oxide produced from the ferrocyanide and ferro-sodium sulphide colours the product yellow, and black spots, from unconsumed carbon, are always present in great quantity. At the best, with good liquors and careful work, the sulphide can be destroyed by conversion into Na_2SO_4, within a hardly appreciable fraction, but only exceptionally the NaOH will be brought down below 2 p.c. of available alkali. Altogether the process of 'carbonating' in *this* manner must be pronounced a very irrational one, although practical experience has brought it to comparative perfection on the Tyne. The reactions taking place in boiling down pans and carbonating furnaces of the Tyneside type have been investigated by Moorhouse (Trans. Newcastle Chem. Soc. 1871, p. 17).

The operation of finishing the soda ash is an entirely mechanical one, even including that of carbonating, wherever this is necessary. After several unsuccessful attempts in this way, Mactear, in 1876, constructed a mechanical carbonating furnace which seems to have solved the problem. It consists of a horizontal circular revolving hearth, 20 feet in diameter, made of boiler-plate lined with fire-brick. It is fixed on a frame fitted with wheels, arranged to run on a circular tramplate beneath the furnace. It is covered by an arch, in which openings are provided for charging the furnace. A double fireplace is built at one end, and a double exit flue at the other end. The discharging takes place by a cylindrical opening in the centre, which is closed by a cylindrical iron valve, jacketed with fire-bricks, and worked from a correspondingly fitted opening in the centre of the roof. Between the two exit flues, and out of the range of the fire, a stirring apparatus is at work, comprising a set of forks, fixed to the lower end of vertical shafts which are held in a frame and are geared together by spur-wheels at their upper ends. The whole stirring apparatus can be raised or lowered by a single movement. The finished charges are pushed towards the central discharge opening by a mechanical arrangement. The connection between the roof and the revolving hearth is made airtight in this way, that the vertical flange of the circular girder, supporting the roof, dips into a gutter, formed outside the rim of the furnace-bottom, and filled with loose soda ash or sand.

The soda ash is thoroughly and continuously turned over every time the slowly revolving furnace-bottom passes underneath the stirring apparatus. It is thus possible to get the caustic down to 0·25 p.c. of NaOH, against the usual 2 p.c. A charge of 3½ tons can be turned out in 6 or 7 hours; the usual turn-out is from 90 to 110 tons in six days. The coal required is 40 p.c. of the weight of the soda ash, without reckoning the steam. There is no saving in fuel as against the hand furnaces, but a considerable saving in labour, compared with the Tyneside carbonating furnaces, six of which are replaced by a Mactear carbonator, and the product of the latter is much superior to that of the former. Where the tank liquors have been carbonated by gas, the advantage of the Mactear furnace is much less conspicuous.

Stuart (S. C. I. 1884, 607) mentions as a drawback of mechanical carbonators that many fluxed pieces are formed, which give much trouble in dissolving the soda ash for making crystals. On the other hand, the ash is better carbonated, it stands more fire in finishing, so that its colour is very much improved, and the oxide of iron is made so dense that it settles out completely in dissolving, and good soda crystals are produced from it very easily. The ash being more dense, there is a saving in casks. The labour is 1*s.* per ton as against 3*s.* in hand furnaces, but since 8½*d.* has to be spent in repairs, and there is more interest on plant, the direct saving by mechanical carbonators is only 1*s.* per ton.

Sometimes soda ash is not calcined at all in the proper sense of the word, but is merely dried at such a temperature that any ferrocyanide present is not decomposed—that is, at a heat not exceeding 150°C. This can be done, for instance, in D-shaped iron retorts, heated by the fire-gases coming from the boiling-down pans, without any expense for fuel. If the liquor had been thoroughly carbonated, so that no Na_2S whatever is present, the above-mentioned process yields a product of great whiteness; the slight proportion of ferrocyanide present is not discoverable by its colour, and is harmless for almost every use of soda—except, perhaps, for glass-making.

Another way of drying soda ash is employed by Hasenclever, at Stolberg, viz. a cast-iron pan, similar to Thelen's evaporating pan (*cf.* above), but here the scrapers, instead of revolving, only oscillate, to avoid dusting, and thus gradually move the salt from one end of the pans, where it is introduced, to the other end. Here it is mechanically scooped out, and is directly charged into the mill, from which (after automatic sifting) it falls into the casks. Such an apparatus dries and grinds 10 tons of soda ash in twenty-four hours, with an expenditure of 1¾–2 cwt. of coals and 10*d.* wages per ton (Chem. Ind. 1880, 240).

Refined alkali. Where the tank liquors are carbonated, and are well settled both before and after this operation, the soda ash obtained on calcining the fished or drained salt is of a white colour, and of sufficient purity for every practical purpose. But where the carbonating is effected by means of sawdust, leaving consequently all the iron and a good deal of caustic in the ash, and adding to it the impurities of the sawdust, the resulting 'yellow carbonate' is not always sufficiently pure, and it is, therefore, sometimes subjected to a process which yields 'refined' or a white 'alkali.'

For this object the soda ash is dissolved in hot water, sometimes with addition of a little bleaching powder, and freed from insoluble impurities by settling, exactly as will be described for the manufacture of soda crystals. The iron, which has been converted into oxide in the calcining process, is left in the sediment. The clear liquor is boiled down in pans, similar to those employed for tank liquor. Where (as is usual on the Tyne) for this purpose pans heated by top fire are employed, the fuel must not be raw coal, on account of the soot and flue-dust, but coke, and experience has shown that it is best to use long pans, say 24 to 27 feet in length, with a coke-fire at each end and an exit flue in the centre. The liquor is boiled down to the consistency of mortar; the salt drained from the mother-liquor is calcined in an ordinary 'finishing-furnace,' and, after grinding, is ready for the market. The loss in this operation should not exceed 5 p.c. of the weight of the soda ash.

'White alkali' should have no yellowish shade, and exhibit no black spots; it should dissolve completely, without any residue, and contain no trace of sulphide or sulphite, or of iron; the caustic, if present at all, should not exceed a fraction of a per cent. Although its manufacture is seemingly a very simple one, it nevertheless requires very great care and attention, and does not yield satisfactory results in every case.

Properties and Analysis of Soda Ash.

Ordinary commercial soda ash should be neither yellow nor reddish, although it is never as white as 'refined alkali,' and, after grinding, should show but few black or red specks. Sometimes it has a blue shade, probably from sodium manganate. Grey ash is badly carbonated and calcined. It should not contain more than 2 p.c. Na_2O in the state of caustic, except when specially manufactured as 'caustic soda-ash' (*v. supra*). Sulphide ought not to be present at all; sulphate only in traces. The insoluble substances should not exceed 1, or at most 1·5, p.c. They consist of calcium carbonate, with a little silica, alumina, and iron. The moisture in fresh soda ash does not exceed $\frac{1}{4}$ or $\frac{1}{2}$ p.c.

Caustic ash has been mentioned above (p. 472) as produced by the French process of direct evaporation in furnaces. It is also produced in the manufacture of caustic soda (*cf. infra*). Mathieson and Hawliczek have constructed an apparatus for manufacturing it from ordinary soda ash and sodium hydrate solution (Eng. Pat. 5,757, 1887).

Soda ash is nearly always *ground*, mostly in horizontal mills, fitted with blue lava stones, and is packed in casks holding from 12 to 20 cwt. The latter weight can be obtained only by means of mechanical packing machines; this is done not merely to save casks, but especially to reduce the bulk for oversea carriage.

The commercial value of soda ash is principally expressed by its *alkalimetrical degree.* This is always tested in the same way—viz., by neutralising the soda with standard acid, which acts not merely upon Na_2CO_3 and NaOH, but also on sodium silicate and aluminate. But the result of the test is expressed differently in different countries. The alkametrical degrees in England mean the percentage of available soda expressed as Na_2O; in Germany as Na_2CO_3 (whether that or NaOH is really present); in France they mean the parts of real sulphuric monohydrate H_2SO_4 required for neutralising 100 parts of the soda ash (Descroizille's degrees). Chemically pure sodium carbonate would show 58·49 English, or 100 German, or 92·45 French degrees. Very frequently, though, the English degrees are not calculated upon the real equivalent of sodium carbonate, which is 53, but upon the arbitrary figure of 54 (Newcastle degrees), and sometimes the deviation is even larger. The following table will allow these various designations to be compared with one another:—

Table for comparing the different alkalimetrical degrees.

Real soda Na_2O	German degrees Na_2CO_3	Newcastle degrees	French degrees	Real soda Na_2O	German degrees Na_2CO_3	Newcastle degrees	French degrees	Real soda Na_2O	German degrees Na_2CO_3	Newcastle degrees	French degrees
1	1·71	1·01	1·58	26	44·46	26·34	41·09	51	87·19	51·67	80·61
2	3·41	2·03	3·16	27	46·17	27·35	42·67	52	88·90	52·68	82·19
3	5·13	3·04	4·74	28	47·88	28·36	44·25	53	90·61	53·70	83·77
4	6·84	4·05	6·32	29	49·59	29·38	45·83	54	92·32	54·71	85·35
5	8·55	5·06	7·90	30	51·29	30·39	47·42	55	94·03	55·72	86·93
6	10·26	6·08	9·48	31	53·00	31·41	49·00	56	95·74	56·74	88·52
7	11·97	7·09	11·06	32	54·71	32·42	50·88	57	97·45	57·75	90·10
8	13·68	8·10	12·64	33	56·42	33·43	52·16	58	99·16	58·76	91·68
9	15·39	9·12	14·22	34	58·13	34·44	53·74	59	100·87	59·77	93·26
10	17·10	10·13	15·81	35	59·84	35·46	55·32	60	102·58	60·79	94·84
11	18·81	11·14	17·39	36	61·55	36·47	56·90	61	104·30	61·80	96·42
12	20·52	12·17	18·97	37	63·26	37·48	58·48	62	106·01	62·82	98·00
13	22·23	13·17	20·55	38	64·97	38·50	60·06	63	107·72	63·83	99·58
14	23·94	14·18	22·13	39	66·68	39·51	61·64	64	109·43	64·84	101·16
15	25·65	15·19	23·71	40	68·39	40·52	63·22	65	111·14	65·85	102·74
16	27·31	16·21	25·29	41	70·10	41·54	64·81	66	112·85	66·87	104·32
17	29·07	17·22	26·87	42	71·81	42·55	66·39	67	114·56	67·88	105·90
18	30·78	18·23	28·45	43	73·52	43·57	67·97	68	116·27	68·89	107·48
19	32·49	19·25	30·03	44	75·23	44·58	69·55	69	117·98	69·91	109·06
20	34·20	20·26	31·61	45	76·94	45·59	71·13	70	119·69	70·92	110·64
21	35·91	21·27	33·19	46	78·66	46·60	72·71	71	121·39	71·93	112·23
22	37·62	22·29	34·77	47	80·37	47·62	74·29	72	123·10	72·95	113·81
23	39·33	23·30	36·35	48	82·07	48·63	75·87	73	124·81	73·96	115·39
24	41·04	24·31	37·93	49	83·78	49·64	77·45	74	126·52	74·97	116·97
25	42·75	25·32	39·51	50	85·48	50·66	79·03	75	128·23	75·99	118·55

Formerly, before all the operations of alkali manufacture were sufficiently perfected, 48 p.c. ash was a very ordinary average, and this has remained the standard of comparison for many English alkali works up to this day, although it would be much more rational to reduce all products of the alkali manufacture to pure sodium carbonate (58·49 English degrees), as is usual in Germany. Nowadays any of the well-conducted works get an average of at least 52 p.c., and the best-managed get up to 54 p.c. or even 55 p.c., some of it in the shape of 57 p.c., and the remainder of lower strength. According to the requirements of buyers, any strength below the highest is obtained by adding common salt to the soda ash, preferably in the drying operation.

As stated above, the alkalimetrical degrees comprise carbonate, caustic, aluminate, and silicate. There is, moreover, always some sodium present as sulphate and chloride. The former may amount to from 2 to 8 or even 10 p.c., the latter from 1 to 3 p.c. These constituents are usually not estimated, as they have no injurious effect, except in lowering the alkalimetrical degree.

Testing soda ash. As a rule, soda ash is merely tested for 'available alkali.' Since a small sample may not exactly represent the average, it is convenient to weigh out 15·5 grms., dissolve in a 500 c.c. flask, and to take for each test 50 c.c., which is sometimes done without filtering (in which case the calcium carbonate, &c., is erroneously calculated as alkali). The standard acid is preferably normal hydrochloric acid, standardised both with pure sodium carbonate and with silver nitrate. The best indicator is methyl-orange, which is used with cold liquors; if litmus is used as indicator, the liquid must be kept boiling for some time, and errors may be caused by alkali taken up from the glass beakers or flasks.

Sometimes a complete analysis is required, in which case the insoluble residue, sodium hydrate, sulphide, sulphite, sulphate, chloride and iron must be estimated (details in Lunge and Hurter's Alkalimakers' Handbook, 2nd edit., p. 138).

Yield and losses. 100 parts of pure sodium sulphate is equivalent to 74·65 of pure Na_2CO_3, or 43·66 of Na_2O. 96 p.c. salt cake would thus correspond to 71·66 Na_2CO_3 or 41·91 Na_2O; but the highest actual yield, as far as it can be reliably ascertained, does not exceed 36·5 Na_2O, and this is but rarely attained. A loss of 15 p.c. of soda must be called a very good practical result; usually it is nearer 20 p.c.

The causes of this loss have been investigated by several authors.[1] They are the following. Some sulphate is carried away mechanically by the draught, and is found in the flues both of the black ash and the finishing furnaces. Some salt is also actually volatilised in the furnaces, and some is absorbed by the furnace bottoms, &c. The sulphate is never quite completely converted into carbonate; with mechanical furnaces this loss is much smaller than with hand-worked furnaces, where it may amount up to 9 p.c. of the sulphate. Even more sulphate is generally re-formed during the keeping of the black ash, and in the lixiviating process, partly passing through the stage of sulphide. A small quantity of sulphite, ferrocyanide, &c., is also regularly formed. Considerable loss is experienced by the impossibility of extracting even all the soluble sodium salts of black ash, and by the constant occurrence of insoluble sodium compounds of various kinds (*cf. supra*). The latter source of loss becomes all the greater the more limestone is employed in mixing, and the more ashes the mixing coal contains, and it may be very serious.

Some loss of available soda is also occasioned by the fact that the sulphurous acid contained in the fire-gases acts upon the sodium carbonate in boiling down and calcining. The amount of this loss has been investigated by Pratt (S. C. I. 1885, 167), but Naef (D. P. J. 256, 513) doubts the correctness of his figures.

Soda crystals. For some purposes soda is required not in the calcined form, as soda ash, but in the crystalline form, in which it contains 10 molecules of water. Although soda crystals, if chemically pure, contain only 37·08 p.c. of anhydrous sodium carbonate, or 21·71 p.c. of available soda (Na_2O), and thus cost much more than their equivalent of soda ash for packages and carriage, they are preferred to the latter in some cases, for the following reasons: while soda ash is a more or less white powder, whose value cannot be recognised at a glance, and which may contain more or less useless, or even injurious, impurities, soda crystals by their very appearance seem to guarantee to the buyer a product of sufficient purity and of uniform strength. Their greatest recommendation for household use, as well as for the scouring of wool and some other purposes, is their absolute freedom from caustic, which is very injurious both to the skin and to the fabrics to be washed or scoured. For all manufacturing purposes soda crystals are now advantageously replaced by ammonia-soda, which is equally free from caustic, and is also of guaranteed uniform strength; but for household purposes the ordinary soda crystals are likely to retain their hold, and are consumed in very large quantities as 'washing soda,' and under various fancy names.

Soda crystals are but rarely obtained directly from tank liquors, even when these have been carbonated, apart from the case of 'crystal carbonate' (comp. this). It is asserted that soda crystals, when made directly from tank liquor (even if by very great care they have been obtained sufficiently pure), are too soft and difficult to sell. The writer has, however, convinced himself that at St. Gobain they are regularly made direct from the tank liquor, after having first oxidised and then carbonated it.

The usual way of preparing them is to dissolve calcined soda ash in hot water, separate the insoluble impurities by a settling process, and cool down the liquor. The soda ash employed need not be of first-class quality, as the impurities mostly remain behind, either in the sediment or in the mother-liquor, but it should be entirely free from sulphide, and should contain a maximum of 2 p.c. Na_2O in the state of caustic soda—preferably less. Caustic soda does not crystallise, and seems to impede the crystallisation of some of the carbonate, so that the yield is very much impaired; apart from that, caustic and sulphide give badly settling liquors and coloured, impure crystals.

Dissolving the soda ash (which can be employed in the unground state) is carried on in several ways. At smaller works it is done by suspending, within an iron tank provided with a steam pipe, a perforated iron box, which dips just below the surface of the liquor in the dissolver. The latter is filled with hot water, and soda ash is thrown into the box, not too much at a time, so that the solution formed sinks down and is replaced by non-saturated liquor. At larger works cylindrical pans, with mechanical agitating gear, are employed—also heated by steam. These do the work much more expeditiously. There are also various plans for continuous work, where solid soda ash is introduced on one side and saturated liquor is run off on the other side.

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[1] Hargreaves, C. N. 15, 219; Wright, *ibid.* 259; Mactear, *ibid.* 25, 54; Scheurer-Kestner, C. R. 70, 1,352; 75, 1,184.

The strength of the liquor in the dissolvers is brought up to 60° or 61°Tw., measured hot; in the settlers at 35°C., it is 66° or 67°Tw. In the case of soda containing an appreciable quantity of sulphide, or of ferro-salts, a little bleaching powder is put into the dissolver, which removes those impurities by oxidation, but naturally causes a loss of soda, as the calcium is entirely precipitated by the latter in the state of carbonate. The soda crystals made in this way sometimes pertinaciously retain a smell of chlorine (caused by the presence of sodium hypochlorite). It is therefore best to avoid this reagent; a small quantity of other oxidising substances—*e.g.* Weldon mud—will effect the purpose better.

The liquor must now be clarified by settling, and this must be done in such manner that the temperature never sinks low enough to allow the soda to crystallise at this stage. This is greatly facilitated by the fact that the maximum solubility of the decahydrated sodium carbonate is at 34°C.; if therefore a strong solution is made at a boiling heat, it has no tendency whatever to crystallise until it has got below 34°C. Hence it is generally sufficient to surround the settlers by bad conductors of heat; but at some works they are actually heated by fire-flues, carried round their sides, but not underneath their bottom, because that would impede the settling. The settlers may be ordinary tanks of various forms, provided with a tap, or, preferably, with a drop-siphon, for running off the clear liquor. Or else they are arranged as described above in connection with the operation of carbonating the liquor—that is, in such number and of such length as to allow of continuous action, so that muddy liquor enters at one end, and completely clear liquor runs out at the other end.

The settled liquor is now run into the 'crystallising vessels,' or 'coolers' (sometimes called 'cones'). Formerly, in England, conical cast-iron pans were used, or such made in the shape of segments of spheres, about 9 feet wide and 2 feet deep, each of which yields 20 to 25 cwt. of crystals. Later on vessels have come into use of a nearly square section, with rounded corners, the bottom sloping to one side, with a plug-hole at the deepest part. When made 8 × 9 × 1 feet, they weigh a little over 4 tons, and yield nearly 1½ tons of crystals each.

The coolers are placed in two or more rows in a shed, kept airy by lattice-work; a gutter for the mother-liquor runs between two rows at the bottom, and an iron shoot runs at the top for charging the coolers with fresh liquor. After the coolers have been filled, several strips of sheet iron are laid over them at right angles to each other, forming a framework to which the crust forming at the top can attach itself, so that very large and fine crystals are formed here. These are always cleaner than those forming at the bottom of the coolers.

In coolers of the size described the crystallisation is finished in about a week in winter, or a fortnight in summer, and in the latter season the yield is always much less, since more alkali remains in the mother-liquor. When the cooling is complete, the top crust is broken, the plug is loosened, the mother-liquor is run out, the crystals are detached from the sides and drained in the vessel itself. Then, or after having been exposed to the air on wooden benches for 24 hours, they are packed into casks without further drying.

At other works (especially on the Continent) the crystallising vessels are large wrought-iron boxes of various sizes, about 2 feet deep. In lieu of the network of hoop-iron on the top, there is a number of strips or rods of iron perpendicularly suspended in the liquor, reaching to about six inches from the bottom in order to form a support to the crystals.

In France it is very usual to employ small iron pots, 14 to 18 inches wide and 8 inches deep, of which there are sometimes thousands placed on a wooden framework. They are filled by means of an india-rubber tube. The crystallisation takes one, or at most two, days (in summer those factories do not work at all). When it is finished the top crust is broken, the mother-liquor is drained off by tilting the whole pot on one side, the pots are then held for a moment in a hot-water pan, till the firmly adhering cake of crystals has been loosened, and this cake is now tilted out, drained for twenty four hours and dried in stoves kept at a temperature of about 20°C.

Commercial soda crystals are not altogether pure, but they usually contain from ½ to 1 p.c. of sodium sulphate and up to ½ p.c. of chloride. They are sometimes adulterated with Glauber's salts, specially manufactured in 'soda-fashion,' and it is said that now and then Glauber's salts are vended as 'best Scotch soda,' but it is hardly credible that such a gross and easily discoverable fraud is frequently committed. On the other hand, it is a fact that crystals made from the very purest carbonate, *e.g.* ammonia ash, do not turn out so well as those made from liquors in which there is enough sodium sulphate to leave about 1 p.c. of it in the crystals.

Mactear (Eng. Pat. 10,651, 1884) has constructed an apparatus for obtaining soda crystals in a granular form, by subjecting the solution during crystallisation to the combined action of cooling by cold-water action from the outside, and mechanical agitation.

In another patent (Eng. Pat. 1,989, 1886) he describes compressing those granular crystals into the shape of tablets, cakes, or blocks, most conveniently of a rectangular form, so that they can be packed without waste of space.

The *mother-liquors* from the crystals are boiled down exactly like ordinary soda liquor, and calcined; they yield very white alkali, but of low strength. Such 'mother alkali' made in winter generally contains about 30 p.c. available Na_2O, in summer from 40 to 45 p.c. (in France 55° Descroizille). There is, of course, a large quantity of sulphate and chloride present, and hence this product, in which only the carbonate is paid for, is in great demand by glass makers.

The yield from 100 tons of 52 p.c. soda ash, deducting the mother alkali (*i.e.* not including it in the 100 tons), at well-conducted English works ranges from 233 to 237 tons of crystals, from 100 tons of ash, 11 tons of mother alkali, of an average strength of 36½ p.c. Na_2O, is obtained.

On the Tyne crystal soda is sold by gross weight—that is, not deducting the tare of the casks. This makes a difference of 7½ p.c. compared with net weight.

Crystal carbonate. This is the name given by Messrs. Gaskell, Deacon & Co. to a very pure monohydrated sodium carbonate, Na_2CO_3,H_2O, obtained by direct evaporation from tank liquors, thoroughly carbonated with addition of bauxite, and afterwards purified from ferrocyanide by superheating to 180°C., as described above (p. 470 and 471). This substance is absolutely free from caustic, silica, and alumina, and is altogether far superior to ordinary soda crystals, not merely in strength, but also in purity, as shown by the following analyses:—

—	Soda crystals	Crystal carbonate
Sodium carbonate . .	34·22	82·90
,, hydrate . .	0·10	0
,, sulphate . .	2·54	trace
,, chloride . .	0·27	trace
Water	62·84	17·00
	99·97	99·90
Total soluble impurities on 100 carbonate .	8·21	0·12
Water on 100 carbonate .	183·64	20·50

Crystal carbonate dissolves in water much more easily than ordinary soda crystals, because, instead of lowering the temperature, it slightly raises it in the act of solution, and because its grainy texture offers a much larger surface to the water than soda crystals do.

One ton of crystal carbonate contains as much alkali as 48 cwt. of soda crystals, and occupies only 65 cubic feet against 150 cubic feet occupied by 48 cwt. of soda crystals.

Bicarbonate of soda. We treat in this place only of the manufacture of bicarbonate of soda from soda crystals, leaving aside its manufacture as an intermediate product in the ammonia-soda process, which will be described further on.

On the small scale—*e.g.* for pharmaceutical purposes—sodium bicarbonate is sometimes obtained by passing carbonic acid into a cold saturated solution of sodium carbonate. The bicarbonate, owing to its lesser solubility, is precipitated in a crystalline form. Most of the bicarbonate found in the trade (apart from that which is made by the ammonia process) is, however, obtained by treating solid crystal soda with carbonic acid gas. This is specially the case with that sold as baking powder, which is the principal application of this article.

The *carbonic acid* is sometimes obtained from the volcanic exhalations containing this gas in a very pure state and in immense quantity; that occurring in the Brohl valley on the Rhine is actually utilised for this purpose. Elsewhere the gas given off in the fermentation of saccharine liquids is used in the same way.

The gas obtained on burning lime or coke, which is quite suitable for the carbonating of tank liquor (*cf.* p. 470) is not adapted for the manufacture of solid sodium bicarbonate, even if purified from SO_2, soot, &c., by washing, because it is too much diluted by nitrogen, &c., which prevents the saturation of the soda with CO_2.

Nearly all bicarbonate is made with comparatively pure carbonic acid, obtained by dissolving limestone in dilute hydrochloric acid, 1 to 7°Tw., such as formerly was run to waste in many alkali works, especially where salt was decomposed by means of open roasters. The apparatus used for this purpose is simply a stone tank, similar to a chlorine still, which is filled with limestone; the hydrochloric acid is run in by a pipe reaching nearly down to the bottom, and the chloride of calcium solution is run off continuously by an overflow pipe near the top. The supply of acid is so regulated that the liquor running off at the top is almost or entirely neutral. The carbonic acid gas is conveyed away by a pipe in the cover of the tank.

The soda commonly employed is in the state of ordinary crystals; those of yellow colour or otherwise inferior quality can be utilised quite well here. They are exposed to the action of the gas in apparatus of various shapes, made of brickwork, wood, or preferably of iron, holding up to 60 tons of crystals. They are connected in such way that the gas passes from one chamber to another. Large doors serve for charging and emptying. A false bottom, made of laths, is laid down inside, below which the gas enters and above which the crystals are put up in regular layers. The space below serves for holding the abundant drainage of mother-liquor caused by the fact that nine of the ten molecules of water of crystallisation are set free:

$$Na_2CO_3,10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

This liquor dissolves the small quantity of foreign salts and other impurities contained in the crystal soda, and runs off through a U-tube fixed in the chamber bottom. The end of the process is indicated by the stoppage of this flow, which generally occurs in from six to nine days. This liquor, on boiling down and calcining, yields very white soda ash of about 36° p.c. Na_2O.

Other tests for the end of the process are: pushing an iron bar through a hole in the side of the chamber, and trying whether it can be got as far as the centre of the chamber without being stopped by hard crusts of soda. Also, dissolving a sample taken from the interior in water and adding mercuric chloride, which ought to produce only a white cloud, not a yellow precipitate.

On opening the chambers the bicarbonate is found apparently in the shape of the crystals originally charged, but in reality only as a loose powder. It is very damp, and must be dried in stoves heated to a temperature not exceeding 45°C. Dry and warm carbonic acid, if not too expensive, would greatly expedite the drying, which generally lasts eight or ten days.

The dry bicarbonate is ground to a very fine powder, as fine as flour, taking care lest the mill gets hot, in which case the bicarbonate loses CO_2. It is packed in barrels holding exactly 1 cwt. net weight.

The ordinary yield is 50 per cent. of the weight of the crystals employed.

A totally different process from that formerly employed is that of Carey, Gaskell and Hürter (1881 and 1882). It is principally based on the employment of the 'crystal carbonate' previously described (p. 478), which is exposed in a revolving cylinder to the action of pure carbonic acid, entering at one end and escaping out of the other; after being passed in a pipe upwards, say 30 feet, and down again, it is sufficiently deprived of moisture, and is re-introduced into the first cylinder, or else into another cylinder. A cylinder of 8 feet length and 5 feet 6 inches wide contains a charge of 1½ tons, and produces 2 tons of bicarbonate. It is movable on hollow journals; gas-pipes pass through these, and upwards inside the cylinder, so that they are not stopped up by the salt. By taking the exit pipe upwards for about thirty feet and down again, and thus evolving the gas, a difference of temperature is produced which effects a sufficient circulation of the gas, while at the same time the excess of moisture is condensed, and the water is run off before the gas passes again into the cylinder. This circulation is in practice best promoted by mechanically pumping the gas back again. The temperature rises very much during the absorption, but the cooling action of the air keeps it down; practically, the bicarbonate made in this way—that is, under a certain pressure—is very strong, containing about 97 p.c. real $NaHCO_3$, against 87–90 p.c. in the old process. The moisture must be regulated; if the mass becomes too dry, the carbonic acid introduced must be moistened by means of a small coke tower. With the progress of absorption the temperature falls again, and it is finished in five or six hours.

The patent contains also provision for employing impure carbonic acid, by passing the gas through a series of absorbing cylinders; but this process does not seem to be in practical use. Anhydrous monocarbonate can also be used (Eng. Pat. 2,876, 1882) by introducing steam together with carbonic acid.

The bicarbonate made by this process had almost superseded that made by the old process, when it was itself displaced by the bicarbonate made in the *ammonia-soda process.* This formerly could not be immediately employed for use as baking powder, &c., owing to the ammonium compounds it contains. Mond and Jarmay (Eng. Pat. 2,996 of 1884) purify it by dissolving it in water at 65°C., which is best done in an atmosphere of CO_2 and under pressure, decanting or filtering, cooling down, and 'centrifuging' the crystals. The cooling is done continuously by conducting the solution through a series of pans, so that the bicarbonate separates out in a granular form. The mother-liquor is used over again, till too much ammonia accumulates, when it is worked up in different ways. Watts and Richards (Eng. Pat. 10,955, 1886) promote the separation of the bicarbonate crystals by adding common salt. Gaskell (Eng. Pat. 11,775 of 1884) purifies such bicarbonate by heating the solid salt in an atmosphere of carbonic acid, in order to drive off the ammonia without losing any CO_2.

The bicarbonate recently found in trade often contains ammonia, also thiosulphate; this can be recognised (Salzer, Ar. Ph. [3] 24, 761) by adding iodine solution, which should not be decolourised. (This test is uncertain, since Na_2CO_3 will do the same.)

Mathieson and Hawliczek (Pat. No. 150, 1886) prepare pure sodium bicarbonate from black ash, crude sodium sulphide, or crude bicarbonate, as obtained in the ammonia-soda process, by dissolving those products in a solution of sodium chloride of from 16 to 19 p.c., and treating the solution with carbon di-oxide, whereby nearly all the bicarbonate is precipitated in a crystalline form. When filtering it by means of a vacuum filter or hydro-extractor and washing it with a small quantity of water, the bicarbonate is said to be obtained nearly in a chemically pure state. With impure materials, as black ash or crude sodium sulphide, the CO_2 first precipitates iron, alumina, and silica, and these are separated by filtration before precipitating the bicarbonate itself.

The principal use of bicarbonate is as *baking powder*, and most of it is exported to America for this purpose. It is used either by itself, or mixed with a solid organic acid or an acid salt; but these mixtures are soon spoiled by attracting atmospheric moisture, which causes the action of the acid to set in before the powder is intended to be used. Horsford and Catlin (U. S. Pat. 270,668) seek to avoid this by moistening the bicarbonate with a magnesium sulphate solution, which coats the former with a covering of magnesium carbonate, and thus protects them against the acid or acid salt. The latter may be tartaric acid, or cream of tartar, or (less appropriately) potassium or sodium bisulphate.

Sodium sesquicarbonate

$$Na_2CO_3,NaHCO_3,2H_2O$$

is made by Watts and Richards (Eng. Pat. 13,001, 1886) by preparing a solution containing the above proportions and allowing it to crystallise not below 35°C., keeping it agitated all the time. Such a solution can be prepared by heating sodium bicarbonate so as to deprive it of about one-third of its carbonic acid and dissolving the residue, or by adding to a hot solution of 84 parts of sodium bicarbonate 106 parts of sodium carbonate. This salt, which crystallises in fine needles, does not effloresce or deliquesce, and is readily soluble in water. Its principal employment is for wool washing.

THE MANUFACTURE OF CAUSTIC SODA.

Solutions of caustic soda have been made ever since soda was commercially used, especially by soap makers; later on by bleachers, paper makers, &c. Most of these prepared such solutions themselves; sometimes they bought them in the state of *caustic liquor*; but from the nature of things this could never be a large trade. Such a trade has only arisen since caustic soda has been manufactured in the *solid* state, which was first done about 1845 in Tennant's works at St. Rollox, but only experimentally. The development of that large industry only dates from 1853, and is intimately connected with the names of Gossage, Dale, Ralston, Gamble, Pauli, Deacon, and other Lancashire manufacturers.[1] Much later it was introduced into the Tyne district and abroad, and it has also acquired great importance in Germany, where the demand for the manufacture of alizarin, of wood pulp, for the purification of mineral oils, &c., served as a stimulus in this direction.

Solid caustic was originally only made from the caustic mother-liquor ('red liquor') obtained in concentrating tank liquor, as before described. This source of caustic is much less important now, since it yields but an impure article, and since many factories carbonate their liquors. Some caustic is made by dissolving and causticising calcined soda ash; but the bulk of it is made from *tank liquors*, obtained in the usual way.

Where caustic is a principal product, this is taken into account even in the manufacture of the black ash, by working up with the ordinary materials such otherwise waste materials as are produced in the further stages of the process, especially the lime-mud from causticising (in lieu of limestone) and the fished salts (which contain both sulphate and carbonate). It is hardly possible to lay down in this case any general rule for the black-ash mixture, as the quality of those by-products is very changeable, and each manufacturer must work out the best proportions for himself.

The black-ash process and the lixiviation are carried out in the usual manner, and the tank liquor is employed for causticising; but generally, either before or after causticising, or along with this, a process for *desulphurising* the liquor is carried out. This can be done in various ways, according to the strength of caustic aimed at. If only ordinary 60 p.c. or 70 p.c. caustic is required, it is sufficient to employ Hargreaves's process of oxidising the sodium sulphide present by injecting air into the liquor, which is either done as a separate operation or in the causticising operation, as will be described below. In this case the oxidation (which is much promoted by heating the liquor) goes only as far as the formation of thiosulphate, and must be supplemented later on by nitrate of soda, or by blowing air into the fused caustic, or both. The same condition is attached to the employment of Pauli's process (Pat. Nos. 1,306 and 1,530 of 1879), which greatly expedites the oxidation by air, by adding to the liquor some 'Weldon mud'—that is, essentially, hydrated peroxide of manganese—in combination with lime, manganese, protoxide, &c. This takes out the sulphur as MnS; but the latter is continuously regenerated into peroxide by the action of air and steam, and would serve an infinite number of times if it did not become contaminated with ferric oxide, silica, and alumina, so that it must be thrown away after having served a number of times. Scheurer-Kestner (Bl. 36, 46) describes a large number of experiments made with Pauli's process on a manufacturing scale. Without addition of Weldon mud, the blowing of a charge corresponding to 1,200 kilos. of sodium carbonate required on an average 7 hours and 6 minutes, and 360 kilos. of coal; with addition of $1\frac{1}{2}$ p.c. manganese on the weight of the soda the blowing averaged only 4 hours 6 minutes, and consumed 204 kilos. of coals—that is, a saving in the proportion of 1·7:1. There is, of course, also, a correspondingly smaller dilution of the liquor by the steam used in the injector. In Pauli's process some of the sulphite is oxidised beyond the state of thiosulphate to sulphate. The total loss of MnO_2 in this process is stated by the inventor to amount to about $\frac{1}{10}$ p.c. of the soda ash.

A detailed description of the oxidising process, both with air alone and according to Pauli's process, has been given by Jurisch (D. P. J. 240, 55). His results are very similar to those obtained by Scheurer-Kestner.

More rational in principle, but more expensive in practice, is the action of zinc or lead oxide, both of them employed as such, or dissolved in caustic soda; instead of converting the sulphide only into thiosulphate, which ultimately passes into sulphate, they convert it into NaOH, and thus admit of producing stronger caustic. In fact, these agents, especially lead oxide, are practically used for manufacturing 'high-strength caustic.' Generally, it is not considered worth while to recover the metal from the ZnS or PbS, mixed with a large quantity of lime mud, as it seems best to use those agents during the causticising itself. Formerly both, especially zinc oxide, were actually recovered from the sulphide (Scheurer-Kestner, *l.c.*); but even then the process costs more than oxidising by air. It is, however, the proper process for making the high-strength caustic (77 p.c.) now so much in demand.

A process patented by Merle in 1875, and carried out at Salindres, consisted in destroying the sodium sulphide in tank liquor by the action of an electric current. Scheurer-Kestner (*l.c.*) found this efficient, but too expensive. It has been patented again by Deacon, Hurter, and Elmore (Pat. No. 800, 1885).

Parnell (Eng. Pat. Nos. 2,203 and 4,188, 1878) has proposed treating the liquor with metallic zinc, which is supposed to remove all sulphide, sulphite, and thiosulphate. Schaeppi (Chem. Zeitung, 1882, p. 1010) has proved that sulphite is not at all, and thiosulphate only partially, acted upon by zinc. Jurisch (D. P. J. 244, 71) comes to a similar result, and concludes that metallic zinc is much inferior in its action to finely-divided zinc oxide.

J. F. Chance (Eng. Pat. 5,920, 1885) decomposes the sulphides by a mixture of ferric hydrate with calcium hydrate or carbonate, produced by precipitating ferric chloride with a large excess of lime or calcium carbonate.

Causticising the liquor. This is done by adding lime to the diluted liquor at a boiling heat with constant agitation. The latter may be brought about either by the blowing in of the steam itself (but this is not sufficient except on a comparatively small scale), or by mechanical agitators, horizontal or vertical, or by blowing in a current of air, divided into very many small jets, by means of a Körting's injector or otherwise. The last-mentioned system requires more steam than mechanical agitation by means of a shaft, but it has the advantage of greater simplicity; and, moreover, oxidises the Na_2S to the stage of thiosulphate, and precipitates most of the iron. It seems to be the prevalent method in England.

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[1] Comp. for the history of the development of the manufacture of caustic soda: Muspratt (S. C. I. 1886, p. 409), Hart (*ibid.* p. 283), Davis (*ibid.* 351).

The tank liquor should be quite as well settled for this purpose as for making soda ash, and should be diluted (with washings from the lime mud, comp. below) to 16° or at most 20°Tw. Above that strength the formation of NaOH is very incomplete, and even at that strength the liquor cannot be altogether causticised, so that as much as 8 p.c. of the Na_2CO_3 present remains as such. As this causes much expenditure of fuel for the evaporation of the dilute liquor, Parnell and Simpson (Pat. Nos. 1877 and 1878) have sought to extend the caustification to more concentrated liquors, by employing a higher temperature, and necessarily a higher pressure, in close steam boilers provided with mechanical agitators. The advantages of their process are, however, doubtful, and it has not at all come into general use. Similar patents have been taken out by Wells (1879), Menzies (1879), Herberts (1882).

Jurisch (Chem. Indust. 1880, 377) has made a very complete investigation of the causticising process, including Parnell's modification of it. Comp. also Lunge and Schmid, B. 1885, p. 3,286.

In the ordinary causticising process the dilute liquor is brought to the boiling-point, and only then (which is considered important) unslaked lime is introduced, placing it within an iron cage which keeps back the stones &c., whilst the calcium hydrate formed is washed out into the agitated liquor and causes the conversion of Na_2CO_3 into NaOH. The end of the process is judged of by practical experience, and, moreover, by filtering a small sample and running the filtrate into dilute acid, which ought not to produce any effervescence.

Generally the liquor is allowed to settle within the causticising pan ('operation pan') itself for half an hour; the clear portion is run off by a swivel pipe, and the lime mud is left in, in order to serve, together with fresh lime, for a second operation. Only then the mud is rejected; but it is first washed in order to obtain the caustic liquor inclosed by it.

The washing of the lime mud is sometimes commenced in the operation-pan itself, or in special settlers, by decantation; but it is always finished on the *mud filters.* These are iron boxes, say 20 × 10 × 4 feet deep; on their bottoms bricks on edge are placed, about 2 inches apart, to form a support for horizontal bricks or porous slabs. These are again covered with a layer of coke or limestone in small pieces, followed by three successive layers of smaller stones and sand, and the whole is covered with cast-iron grids to enable the men to work about with spades without disturbing the filter. The whole of these layers occupies 2 feet depth, leaving another 2 feet for the muddy liquor. Of course, in lieu of the just described filtering layers, other means may be employed for the same end.

Solvay (Eng. Pat. 8,723, 1885) covers the filter with several layers of asbestos cloth. A very good filter, acting under pressure, has been constructed by Herberts (Eng. Pat. 3,537, 1882).

Other filters have been patented by Bolton and Wylde (No. 5,403, 1883) and Bolton and Bullough (No. 14,563, 1888).

Since the filtration would otherwise be too slow, it is generally assisted by connecting the space at the bottom of the filter with a vessel in which a vacuum is produced by means of an air-pump. In this case, as soon as the supernatant liquor is drawn off and the mud exposed to the air, cracks are formed, which would admit air and destroy the vacuum if they were not continuously filled up by turning up the surface of the mud either by hand or by machinery. When the first liquor has run off, water is run on and allowed to stand a little on the mud before drawing it off again, and this is repeated so long as the water takes up an appreciable quantity of soda. These washings are utilised for diluting the tank liquor previous to causticising.

In France they sometimes employ, in lieu of such filters, a series of tanks placed one above the other, where the lime mud is washed by decantation, the washings being employed as usual for diluting the tank liquor previous to causticising (Scheurer-Kestner, Bl. 36, 415).

Even washed lime mud always retains some available soda, part of it in the free state and part in chemical combination with calcium carbonate, as 'gay-lussite,' $CaCO_3 + Na_2CO_3,5aq$. The wet mud generally contains about 2 p.c., but sometimes 4 p.c. or even more, of Na_2O; this causes a loss of $\frac{1}{2}$ to $\frac{3}{4}$ cwt. of Na_2O per ton of caustic, or even more with inferior lime, of which a larger quantity is required (Watson Smith and Liddle, C. N. 43, 7; S. C. I. 1880, 377).

Wet lime mud may be assumed to contain about half its weight of water; the lime is mostly present as carbonate, but a few per cents. of caustic lime are never absent.

The utilisation of lime mud is usually effected by employing it (in the damp state) for replacing part of the limestone in the black-ash mixture; but it cannot be denied that this is not very desirable for the process. It has also been tried to dry it and burn it again; but this is usually too troublesome and expensive. Recently very good cement has been made of this lime mud (Rigby, S. C. I. 1888, 301).

The analyses of factory products on next page (by Lunge and Smith, S. C. I. 1883, 525), will give an idea of the composition of the liquor before and after causticising; but the less important constituents, as silica, alumina, and iron, were not estimated. The figures indicate grms. per litre.

Analyses of liquors, lime mud, &c., are also given by Davis (C. N. 32, 187), and Jurisch (Chem. Ind. 1880, p. 241 and 377).

A totally different method of causticising is that of Löwig (Eng. Pat. 4,364, 1882), who evaporates soda liquors with pure ferric oxide, and exposes the mixture to a bright-red heat. The mass is thus converted into sodium ferrate (or rather 'ferrite'), which is insoluble in cold water, so that it can be purified by washing with it: it is then treated with water at 80°C., which

Analyses of factory products.

—	A		B	
	a Liquor desulphurised by blowing with air, sp.gr. 1·302, at 24°C. grms.	*b* Similar liquor, diluted and causticised, sp.gr. 1·1338 at 20°C. grms.	*c* Another liquor, not previously desulphurised, sp.gr. 1·113, at 24°C. grms.	*d* Similar liquor, causticised by mechanical agitation, sp.gr. 1·103 at 26°C. grms.
Sodium hydrate . .	52·0	102·5	41·1	80·7
„ carbonate .	295·1	32·9	59·0	8·6
„ chloride . .	3·1	1·4	2·5	2·5
„ sulphide . .	—	—	1·3	1·3
„ thiosulphate	5·7	2·9	1·3	2·3
„ sulphite . .	—	—	8·6	6·5
„ sulphate . .	4·5	2·5	8·2	8·3
Water by diff. . . .	941·3	991·6	991·0	992·8
Total	1302·0	1133·8	1113·0	1103·0

decomposes the compound into caustic soda and regenerates the ferric oxide. Thus concentrated liquors are obtained quite free from iron. In a new patent (Germ. Pat. 41,990) Löwig extends this plan to the sodium bicarbonate of the ammonia-soda process, which is first heated in a closed apparatus till half of the CO_2 and all NH_3 are expelled, and then further in a revolving furnace till the whole has been converted into a compound of soda with ferric oxide, which is split up by the action of water into caustic soda and insoluble ferric oxide. The British patent of Mond and Hewitt (No. 1,974 of 1887) amounts to the same thing. Löwig's process has the advantage of yielding much more concentrated liquors than causticising by lime, but the extra expense very nearly swallows up the profit arising from that cause. It has found a certain, but not very extended, practical application in the manufacture of caustic from ammonia soda ash.

The *concentration* of the caustic liquor is a very important part of the process, and causes much of its expense. Attempts have been made (first by J. Dale; *cf.* p. 472) to save fuel by effecting the first part of the concentration—say, up to 48°–50°Tw.—in a steam boiler, and utilising the steam for various purposes; but these attempts have been given up again almost everywhere, because the steam boilers are very much corroded, and any leaks produce very awkward consequences. In connection with the Honigmann caustic soda locomotive engine (propelled without fire during its active work, by means of the latent heat accumulated in a boiling strong solution of caustic soda), these attempts have been taken up again and vigorously pursued; but iron has been found to stand the liquor very badly, and even with copper boilers there are great difficulties. The corrosion of the boilers is, no doubt, principally caused by sodium sulphide; but sodium hydrate itself is not without action upon iron at the temperatures in question (*cf.*, for instance, Lunge, Chem. Indust. 1886, 49; Venator, *ibid.* 144). Where caustic soda is made from ammonia soda, in which case it is entirely free from sulphides, it has been found possible to concentrate in steam-boilers or 'multiple-effect' evaporators.

In ordinary cases the concentration of the liquor is, from the first, carried on in pans heated by the waste heat of the black-ash furnace, as far as this will go; but it is never sufficient to finish the concentration by waste heat alone, and some of the pans must be provided with fireplaces of their own. So long as the concentration has not attained that point where salts begin to separate, ordinary flat-bottomed pans may be employed; from that point on 'boat-pans' must be employed, as described above. These boat-pans are sometimes made of cast iron, but more usually of wrought iron. They are fixed behind the ball furnaces in the usual way, and are so arranged that the pan receiving the liquor directly from the filters is set at the highest level, and the strong pans are fed from the weaker ones by natural gravitation.

It is not possible to lay down rules for concentrating the caustic liquor and treating the salts applicable to all cases, since very much depends upon the purity of the liquor, which varies to a great extent. Impure liquors begin to salt out not much above 50°Tw.; purer ones only at 70°Tw., when the thermometer indicates about 138°C. Some manufacturers stop the firing at this point; others go on to 80° or 85°Tw., or even nearly to 100°Tw., before drawing the fire, and allowing the liquor to settle for ½ to 2 hours. Part of the salt is fished out during evaporation, and part of it is obtained as a muddy deposit in the settlers. The fished salts consist principally of sodium carbonate and sulphate, mixed, of course, with sodium hydrate and with all impurities, especially sulphite and thiosulphate, but very little chloride. The salt from the settlers (which is much less abundant), sometimes, according to G. E. Davis, contains a large proportion of chloride, with all the other salts mentioned above; but this is not general, as will appear directly.

The *settling* of the liquor before it goes from the boiling-down pans to the caustic pots is of very great importance. The longer and more carefully this process is carried out—for which purpose, of course, sufficient tank-room must be provided—the higher will be the strength of the caustic soda manufactured; indeed, the principal part of the secret of making 'high-strength caustic' lies here.

Bolton and Wylde (Eng. Pat. 15,624, 1888) separate the suspended matters by mineral filter-beds, whereupon they are fit to be treated in 'multiple-effect' evaporators, without fear of stopping them up.

The following analyses (by Lunge and Smith) will give an idea of the composition of the liquors and of the salts at this stage of the process. The figures refer to grms. per litre of the liquid and per kilogram of the salts; *a* is the liquor A (comp. above) boiled down to sp.gr. 1·5417 at 18½°C., and 150°C. boiling-point, after having received some nitre (see below), and having been settled; *b* is the fished salts, obtained during the boiling down to the stage *a*; *c* are the salts found in the settler as a brown, pasty mass; *d* is the liquor B (comp. above) concentrated to the point of adding nitre (this liquor had not been treated by injecting air)—that is, to sp.gr. 1·182 at 23°C., boiling-point 114°C.; *e* the same liquor, with addition of about 1 part nitre to 100 of total solids, concentrated to sp.gr. 1·4087 at 23°C., and 140°C. boiling-point, ready for the finishing pot; *f* is the salts fished while bringing *d* to the stage *e*. These liquors and salts are from two different German works evidently very carefully conducted, as appears from the small amount of chloride and sulphate and the great concentration attained before settling. Alumina and silica were not estimated in these analyses.[1]

—	*a*	*b*	*c*	*d*	*e*	*f*
Sodium hydrate . .	751·6	261·2	283·9	139·5	605·4	216·3
„ carbonate . .	34·1	365·6	241·1	19·4	43·5	140·6
„ chloride . .	10·6	5·2	4·4	4·6	24·8	11·8
„ sulphide . .	—	—	—	2·8	trace	—
„ thiosulphate .	10·6	5·6	6·0	2·0	8·6	—
„ sulphite . .	5·6	4·1	71·1	17·1	8·3	178·0
„ sulphate . .	2·5	38·9	92·1	17·2	1·5	165·7
„ nitrite . .	4·7	—	—	—	6·7	3·3
Insoluble (chiefly Fe_2O_3) .	—	1·0	6·2	—	—	1·5
Water (by difference) .	722·0	318·5	295·2	979·4	781·9	282·8
Total . . .	1541·7	1000·0	1000·0	1182·0	1480·7	1000·0

The salts are always worked up by mixing them with the salt cake in black-ash making. Sometimes they are previously washed with partly concentrated liquor, to extract some of the caustic. If they contain a large portion of sodium chloride, they are better kept out, as they would deteriorate the quality of the black ash.

Usually the addition of *Sodium nitrate* which is practised to some extent at nearly all caustic soda works, is made during the boiling-down process. Of course, where the liquor has been oxidised by air, much less nitre is required than where the latter has to perform the oxidation altogether; and where the oxidation is completed during fusion itself by a current of air, naturally even more nitre is saved; but generally a little nitre is used even in that case. While all investigators agree that oxidation by air in dilute liquors converts the sulphide only into thiosulphate, opinions widely differ concerning the oxidation by nitre and that effected by air at a high temperature. Pauli assumed that up to a boiling-point of 138°–143°C. the sulphide is oxidised into sulphate, and the nitrate reduced to nitrite; between 143° and 150°C. the nitre is reduced to ammonia, above 155° to nitrogen. G. E. Davis asserts that even below 138° much ammonia is given off; this stops mostly at 182°, when nitrogen takes its place. The sulphide he believes to pass through the stages of thiosulphate and sulphite into that of sulphate. Parnell denies the formation of any nitrite or ammonia. This matter has been completely investigated by Lunge and J. H. Smith,[2] who proved that all previous assumptions were partly or entirely wrong, and that the reactions are as follows: under no circumstances is nitrate reduced directly to a lower form than that of nitrite. In this first stage it is capable of oxidising sulphide to sulphite, and this to sulphate, from about 140°C.; but thiosulphate is not acted upon as such either by nitrate or nitrite. Nitrite itself oxidises sulphide to sulphite, chiefly with reduction to ammonia, at temperatures from about 200°C. At very high temperatures, exceeding 360°, sulphite is oxidised into sulphate, the nitrite being chiefly reduced to nitrogen. The thiosulphate formed previously by the action of air (but not of nitrate) on the sulphide is split up at higher temperatures in the presence of caustic soda, with reformation of sulphate and reproduction of sulphide (as might be concluded from its molecular structure):

$$SO_2(ONa)(SNa) + 2NaOH$$
$$= SO_4Na_2 + Na_2S + H_2O.$$

The sulphide is now, of course, acted upon by nitrate and nitrite as above; but this is done only gradually, as the decomposition of thiosulphate goes on but slowly. All these reactions go on in glass or porcelain vessels, without any iron being present; if this is the case (as it always is in practical work), the reactions remain exactly the same, but they take place at somewhat lower temperatures.

The practical conclusions drawn from those experiments are, that it is best to commence the oxidation by blowing (before and during causticising). This saves nitre, and also preserves the iron vessels from being too much corroded. Then some nitre should be added, but not too much, so that its work is done principally below 300°, or at least 360°; in this case it is converted into ammonia, in accordance with the equation:

$$NaNO_3 + 2H_2O = NaOH + NH_3 + O_4,$$

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[1] Other analyses are given by Davis (C. N. vol. 32, *passim*) and Jurisch (comp. above).

[2] S. C. I. 1883, 460, 525.

while at a higher temperature, when most of the water has been driven off, the less favourable reaction takes place:

$$2NaNO_3 + HOH = 2NaOH + N_2 + O_5.$$

It is, therefore, best to complete the oxidation in the finishing pot by injecting air into the caustic, then existing in the state of fusion at a red heat.

Where white caustic has to be made from red liquor, it is not possible to economise the nitrate in the manner just mentioned. The following is a rule for making very white caustic from red liquor: Boil down the liquor to 35°Tw. with the waste heat from the revolvers; continue boiling down, with addition of some nitre, to 100°Tw. in a boat-pan, fishing out the salt; allow the liquor to settle, and bale the clear portion into the finishing pot. Here it is brought to 480°C., when three-quarters of the final nitre is put in and the temperature is now raised to 700–730°C. The mass is now allowed to settle, and *only then* is the last quarter of the nitre put in. The settling takes place much more thoroughly *before* the last nitre is added, a fact considered to be a very important manufacturing secret. The longer the heat is kept at 700°C. the more salts settle out; therefore this is done a longer time for 70 p.c. caustic than for 60 p.c. Before packing, the mass is allowed to cool down to 340°.

At the Aussig works the operation of adding the nitre is conducted in such a way that the ammonia formed can be condensed and utilised. This is considered not to pay by the majority of works.

The last stage of the manufacture of caustic soda is performed in the *finishing pots*, which are shown in fig. 41. These are castings of superior quality, from 7 to 9 feet wide and 4 to 5½ feet deep, and 2 inches, or, more usually, 3 inches thick. The larger pots hold about 10 tons of caustic; if properly set and treated they last about two years, and turn out 600 or 700 tons of caustic. They must be set so as not to receive the sharpest heat of the fire, *e.g.*, with a curtain wall over the fireplace, and they are generally placed on an iron plate, so that they can be turned a little every three months, and fresh places are exposed to the fire. They are provided with sheet-iron covers, balanced by a chain, pulley, and weight, which are used in the last stage of the process.

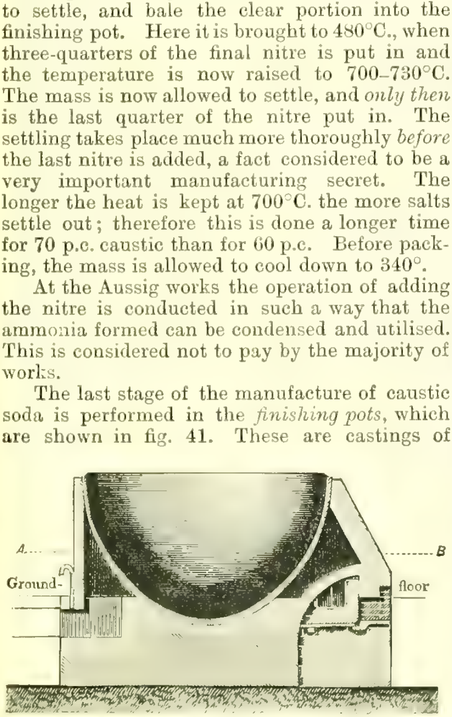

FIG. 41.

At different works they operate very differently as far as the strength of liquor for charging the pots is concerned. Sometimes liquor boiling at 138° is used, so that much of the salting-out must be done in the pots; but it seems preferable to do this in the boat-pans and charge the finishing pots with much stronger liquor, boiling at 160°C. (comp. the analyses above). This latter course is especially advisable when aiming at 70 p.c. caustic.

The pots are first fired sharply, till the boiling-point has reached 180°C.; the liquor on cooling will now solidify to caustic of 53 p.c. Na_2O. From this point it is tough, and shows a great tendency to boil over, which must be kept down by beating down the froth with a shovel. About 205°C. the boiling becomes very slow; at 238°C. the mass contains almost exactly 60 p.c., at 260° about 64 p.c., alkali. There is now a very pungent atmosphere round the pot, caused by minute particles of caustic carried away by the liquor, and the surface of the mass is covered by a shining coat of graphite, formerly ascribed to the destruction of the cyanide but now proved to be caused by the action of the caustic on the cast-iron pot itself (Thalheim, Chem. Indust. 1880, 53).

At this stage the last oxidation of the caustic is brought about, either by throwing on, very cautiously, a few pounds of nitrate of soda at a time, or by blowing a current of air into the fused mass by means of a movable pipe, 1½ inches wide, ending below in a perforated branch or ring. Eight hours' blowing suffices for good caustic, each ton of which requires from 24,000 to 30,000 cubic feet of air; bad liquor requires much more than that.

By blowing, Na_2S is converted into Na_2SO_4, and as in using nitrate the latter is converted into NaOH, the caustic will be somewhat stronger in the latter case. Whether oxidation by blowing or by nitre is more economical is a local question, but the majority of works employ the former process, which is also preferred for this stage by Lunge and Smith (comp. above). Without blowing, from ½ to 1 cwt. of nitre is required for one ton of white caustic.

Whichever way of oxidising the caustic may be employed, a trace of unoxidised sulphur is purposely left in, because otherwise green sodium manganate is formed. If this has inadvertently taken place, the green colour is destroyed by adding a very little sulphur or sodium thiosulphate.

When the oxidation is finished, a sample is taken out and tested. Even if 60 p.c. caustic is aimed at, the sample should test *at least* 64 p.c., preferably more; it is brought down to 60 by adding the requisite quantity of common salt, previously dried in a furnace, to prevent decrepitation on throwing it in. It is indispensable to get the mass up to at least 64 p.c., because otherwise the ferric oxide, alumina, &c., would not become insoluble.

The next operation is the *settling* in the pot, first patented by Ralston; that is, keeping the fused mass heated in the pot for eight or twelve hours, without allowing it to boil, so that the precipitate formed can settle down to the bottom. This precipitate consists of ferric oxide, alumina, and silica, which are soluble in aqueous caustic liquor, but insoluble in caustic soda in the state of igneous fusion. These impurities are thus found in the 'bottoms,' and the upper portions of the contents of the pot are perfectly limpid and white.

The *packing* of the caustic consists in ladling it into *drums*, cylindrical sheet-iron casks, 1 foot 8 inches wide and 2 feet 8 inches high, holding about 6 cwt. of caustic. At the top there is a hole for filling, closed by a cast-iron slide. The drums are usually placed all round the pot, and are successively filled by means of a shoot, into which the liquid caustic is baled from the pot. An excellent arrangement is this: setting all the finishing pots in a row, and laying down a tram-line on one side, on which small wooden platforms (bogies), each carrying a drum, can be moved about at will. In this case the shoot always remains in the same place, and the drums are successively brought under it by means of these bogies.

In America a very large quantity of caustic is sold for household use in tin canisters of 1 lb. each, or in balls covered with a coating material. Péchiney has described a machine for moulding caustic soda in small pieces (Eng. Pat. 2,478, 1885); M. E. Brigham a machine for moulding it into balls (U. S. Pat. 260,832); B. T. Babbitt (U. S. Pat. 256,095) describes the way in which tin drums can be fitted without being first soldered.

Sometimes the caustic is ground in mills; comp. patents by Menzies (1879), and Pitt (Eng. Pat. 4,677, 1883). At Salindres there is an apparatus, invented by Boulouvard, for converting caustic soda into thin scales; it consists of two drums, revolving in opposite directions, internally cooled by water. Liquid caustic is run on to the drums, where it solidifies instantaneously and detaches itself in thin flakes.

When in packing the lower portion of the pot is reached, great care must be taken not to disturb the sediment. As soon as the mass becomes of doubtful quality, it is baled over into a neighbouring pot, till the dark-red 'bottoms' are reached. These are either packed in special drums and sold in this state (generally on the basis of 54 p.c. alkali), or they are dissolved in hot water, when the ferric oxide and other foreign matter settles out, and the liquor is worked up with other caustic liquor.

Cream caustic. This is an inferior quality, sometimes made from tank liquor, but mostly from red liquor—*i.e.* the caustic mother-liquor remaining behind when non-carbonated tank liquor is worked up for soda ash. Such red liquor contains per litre nearly 200 grms. NaOH, together with about 80 grms. Na_2CO_3, and considerable quantities of all other sodium compounds occurring in tank liquor; also in every case some iron sulphide. It is boiled down in boat-pans till about 94°Tw., or 132°C. boiling-point, has been reached, when it is ready, after settling, for the finishing pot. During the concentration the salts are fished out, and nitrate of soda is added, of which sometimes more than 3 cwt. per ton of caustic is needed; blowing in the fused state is not applicable in this case, because the temperature does not get high enough. The concentration is continued till the strength has come up to 60 p.c., at which the whole contents of the pot are packed into drums right away, without any settling (which would not take place to any extent), and consequently without any 'bottoms.'

The following analyses (Chemical Trade Journal, 1888, 86) show the composition of ordinary trade products :—

—	Red liquor cream	Vat liquor cream	60 p.c. white	70 p.c. white	Caustic bottoms	High-strength caustic
Water	9·0	12·3	—	—	—	—
Insoluble . . .	0·2	—	—	—	23·0	—
Sodium chloride . .	6·8	7·8	15·1	3·9	6·1	1·3
,, sulphate . .	1·5	2·2	3·6	3·4	5·5	1·5
,, sulphite . .	1·5	0·1	—	—	0·2	—
,, silicate . .	2·1	0·2	0·1	0·3	0·7	0·1
,, aluminate . .	0·8	1·3	0·4	0·2	5·6	0·2
,, carbonate . .	3·1	1·4	1·1	2·4	—	0·2
,, caustic . .	75·0	74·6	79·8	89·6	58·6	96·0

The author's own analyses of German high strength caustic show:

—	Made by Solvay from ammonia ash	Made at Heufeld	Made at Ludwigshafen
Total alkali (real Na_2O) . .	74·92	73·45	74·67
Sodium hydrate	94·88	92·34	94·60
,, carbonate	2·38	3·10	2·27
,, sulphide	0	0·01	0
,, sulphate	0·19	2·82	2·82
,, chloride	1·69	1·71	0·51
Alumina	0	trace	0
Iron	0	0	0

The Utilisation of Soda Waste.

Soda waste (alkali waste, tank waste, vat waste), the product remaining behind in the lixiviation of black ash, is a dark-grey or black granular mass, mixed with coarser particles and fine mud. The published analyses of this substance are nearly all useless, as they refer to it in a state changed by exposure to air. This was avoided in an analysis by Lunge (Lunge's Sulphuric Acid and Alkali, ii. 635), which was made with perfectly fresh waste, and which yielded: sodium carbonate (partly in the soluble and partly in the insoluble state, or gay-lussite) 3·95; calcium sulphide, 39·42; calcium hydrate, 9·95; calcium carbonate, 22·64; calcium silicate, 3·19; calcium sulphate and thiosulphate, traces; ferrous sulphide, 3·07; alumina, 0·76; coke, 2·36; sand, cinders, &c., 13·72; water and loss, 0·94.

The following more recent analyses, given in A. M. Chance's paper in the S. C. I. 1882, 266, give a very good idea of the composition of soda waste obtained with different mixings, and both from hand-worked and mechanical black-ash furnaces:—

—	Names of firms and description of furnaces									
	Gaskell, Deacon and Co. revolver	British Alkali Works revolver	Netham Chemical works revolver	Radcliffe Chemical works revolver	Muspratt (Widnes) hand	Jarrow Chemical Co. revolver	Tennant's (Glasgow) revolver	Gamble St. Helens hand	Chance Brothers hand	
									a	*b*
Salt cake used for mixing	100·0	100·0	100·0	100·00	—	100·00	—	100·0	100·0	100·0
Limestone used for mixing	86·0	86·0	95·5	105·00	—	100·00	—	105·0	105·0	105·0
Coal used for mixing	40–42	40·0	53·4	33·33	—	57·00	—	57·5	65·0	65·0
Sulphur										
Total percentage in waste	26·33	24·29	23·52	22·66	20·73	17·94	18·84	19·47	17·22	18·01
Recoverable	25·28	23·87	23·10	21·30	19·87	17·83	17·59	17·17	15·59	16·83
Percent. recoverable	96·02	98·27	98·21	94·00	95·85	99·39	93·36	88·19	90·53	93·29
Na_2CO_3	3·16	2·57	—	0·45	—	—	—	3·69	1·63	1·97
Na_2O	—	—	1·47	—	—	—	1·17	—	—	—
NaOH	—	—	—	—	—	1·88	—	—	—	—
$CaCO_3$	21·19	28·10	20·07	38·14	35·26	27·92	28·41	23·64	38·81	36·92
$Ca(OH)_2$	trace	—	5·92	7·62	—	8·60	4·90	8·89	9·53	8·85
CaS	56·89	53·77	52·03	47·97	44·75	40·16	39·62	38·67	35·12	37·90
CaS_2O_3	1·07	—	—	—	–	—	1·19	2·85	1·49	0·68
$CaSO_3$	trace	—	—	—	—	—	—	—	—	—
$CaSO_4$	trace	—	trace	—	3·76	—	2·13	0·91	—	0·20
$CaSiO_3$	3·53	1·47	—	—	—	2·96	—	4·19	—	—
Coal	7·20	9·62	13·69	0·30	5·72	12·33	8·03	5·86	6·27	7·04
$MgCO_3$	—	—	—	—	—	—	1·35	0·98	—	—
MgO	—	—	0·60	—	0·42	2·13	—	—	—	trace
Al_2O_3	1·02	0·74	1·98	—	2·45	2·13	8·62	1·01	0·13	0·34
FeS	1·65	1·16	1·16	3·74	—	0·29	0·70	2·46	2·76	2·44
Fe_2O_3	—	—	—	—	1·64	—	—	—	—	—
SiO_2 (chemically combined)	—	—	1·50	—	—	—	—	—	1·21	1·34
Sand	2·82	0·89	2·09	2·51	6·00	0·66	3·98	7·41	2·61	1·79
Total	98·53	98·32	100·51	100·73	100·00	99·06	100·10	100·56	99·56	99·47
Percentage of moisture in fresh waste	29·20	29·41	27·50	—	—	—	—	—	30·40	29·96

The damp waste, as it is cast out of the tanks, is at once acted upon by the moisture, carbonic acid, and oxygen of the air, and is quickly changed. The action is accompanied by the evolution of much heat, and of a large quantity of gas, especially hydrogen sulphide. If the temperature rises to the combustion-point of this and of the sulphur formed at the same time, fumes of sulphur dioxide are given out. The atmospheric and subsoil water dissolve some of the products of the action, and produce a yellow or red fœtid liquor, which is an intolerable nuisance, both by itself and when discharged into public watercourses. All this lasts a long time before the action is complete, and the mass is converted into an innocuous mixture of sulphates, carbonates, &c. Where large heaps of soda waste are collected, even after thirty or forty years, unoxidised sulphur is found in the interior parts.

Owing to the above-described nuisance, soda waste is never allowed to be simply thrown on to any waste ground, much less to be mixed with any other refuse, which only intensifies the processes described. Formerly the great majority of works disposed of it by keeping it apart, spreading it into thin layers, and beating these down with a shovel, putting layer upon layer till large banks are formed. These, however, in course of time give rise to the same nuisance, especially in damp weather; nor is this at all sufficiently prevented by covering up old waste heaps with ordinary soil. Another plan is preferable; taking out the soil to a depth of several yards, depositing the waste in the hole thus formed to within a few feet of the ground level, and filling up the remainder with part of the soil previously removed. But even with this plan, the greatest nuisance caused by the waste, the infection of the subsoil drainage, will remain in most cases. Altogether, the fact that in the tank waste the sulphur originally imported into the Leblanc process is not merely lost, but is the cause of extreme annoyance to all residents near the works, if not of actual damage to health and life, is one of the most serious drawbacks of that process.

The nuisance caused by tank waste has been minutely investigated by Dr. Ballard (Eighth Annual Report of the Local Government Board, supplement containing the Report of the Medical Officer for 1878, p. 201-226). It seems certain that there is an injurious effect on the health of the neighbourhood caused by the evolution of hydrogen sulphide from heaps of tank-waste, although it is not as bad as is sometimes imagined, especially by those not used to the nauseous smell prevailing in their neighbourhood.

Where alkali works are situate in immediate and near communication with the sea, as is the case on the Tyne, the waste is put into specially-constructed barges, called 'hoppers,' and is sent out to sea, where it is discharged by means of a trap-door in the bottom of the barge. This is a somewhat costly process, and in stormy weather, when the 'hoppers' cannot be taken out to sea, it causes great inconvenience. In places remote from the sea, this way of disposing of the waste is out of the question, and it is usually deposited in heaps, which in some places have taken up an enormous space. According to the Alkali Inspector's 23rd Report for the year 1886, p. 64, 387,000 tons of waste were laid down in that year at Widnes and Runcorn. These would contain about 58,000 tons of sulphur, of which only 4,000 tons were recovered by Mond's process (see below). There were in that year more than five millions of tons of waste lying at Widnes (comp. 21st Report, p. 10).

Many uses have been proposed for soda-waste: for making floors in dry places; for working it up with asphalt for mastic pavement; for mixing with mortar in building; for making bottle-glass; as a remedy against dry-rot and other plant diseases caused by fungi &c. But none of these can dispose of a large quantity of waste, and the largest portion of the 2 tons of wet, or 1½ tons of dry, waste, turned out for each ton of soda ash remains as a burden to the manufacturer.

Evidently the only rational way of dealing with soda waste is to take out of it in some shape or another the sulphur which is the cause of all the trouble, and which at the same time is the most costly ingredient of the Leblanc process (apart from the small quantity of nitre employed). If all European alkali works recovered all the sulphur used in the manufacture of soda, this would amount to 180,000 tons per annum, or about half the total production of sulphur in Sicily; and if all the English Leblanc works recovered their sulphur, this would yield about 60,000 tons per annum, or about twice the yearly importation of brimstone from Sicily into England. A very large number of patents have been taken out with this view, but very few of them have been even partially successful, and only these will be described here in some detail. Of the others we shall only say a few words.

J. L. Bell (1852) made 'factitious pyrites' by smelting tank waste with burnt pyrites, coke and clay, the latter in order to form a slag with the lime. Iron sulphide was formed and tapped from time to time, but this product was very poor (30·6 p.c. sulphur) and difficult to work.

Ward (1862) ignites tank waste with salt-cake to form a double compound of sodium and calcium (probably of very little use).

Hewitt (1877) heats tank waste with silica, whereby calcium silicate is formed and the sulphur is drawn off as SO_2 or SO_3.

Kynaston (Eng. Pat. 2,473, 1885) treats alkali waste for the recovery of sulphur and calcium sulphite, by the assistance of magnesium chloride, in a somewhat complicated way.

Parnell and Simpson's process of utilising soda waste for decomposing the ammonium chloride liquor of the ammonia-soda process will be described in the latter section.

The only way in which, until quite lately, soda waste has been successfully deprived of at least a portion of its sulphur, and has at the same time been rendered entirely harmless, is that first attempted by Leighton in 1836. He allowed the waste to oxidise[1] in the air for some time, lixiviated it, and precipitated the sulphur from the liquor by hydrochloric acid. In 1852 Losh patented the manufacture of sodium thiosulphate from the liquors obtained from oxidised tank waste. Further progress was made in 1860 and 1861 by Townsend and Walker, by Jullion and by Noble. But only in 1862 two inventors simultaneously (after previous trials), but altogether independently, arrived at practicable methods for recovering the sulphur from soda waste, Schaffner and Mond; the process of the latter, with some of the features of the former, has been carried out at a number of English and Continental alkali works, and will be described subsequently.

First, however, we shall describe the changes brought about in soda waste, either in a gradual manner by simple exposure to the air, or hastened by blowing air through it. It was formerly assumed that in this case both oxygen and carbonic acid are acting together with water in the following way: $2CaS + O$ forms $CaO + CaS_2$, the latter combines with O to form CaS_2O_3 which afterwards splits up into $CaSO_3 + S$, and at last $CaSO_4$ is formed. The two last reactions lead to a loss, since $CaSO_3$ and $CaSO_4$ are insoluble and worthless, but they unavoidably take place to a considerable extent. The CO_2 acts by expelling H_2S, which partly combines with CaS to form soluble $Ca(SH)_2$, and is partly converted by O into H_2O and S. The sulphur, set free by this and other reactions, combines with S to form soluble polysulphides. This represents Schaffner's views, which have been proved to be untenable by Divers. More correctly Kraushaar (D. P. J. 226, 412) maintained that the primary reaction is a simple hydration process:

$$2CaS + 2H_2O = Ca(SH)_2 + Ca(OH)_2.$$

The calcium sulphydrate later on combines with oxygen, and forms polysulphides:

$$Ca(SH)_2 + O = CaS_2 + H_2O,$$

and thiosulphate: $Ca(SH)_2 + O_4 = CaS_2O_3 + H_2O$ or more probably, $CaS_2 + O_3 = CaS_2O_3$. By avoiding the action of oxygen, more sulphydrate is formed, and by employing steam at five atmospheres pressure, up to 90 p.c. of the sulphur can thus be brought in solution.

Kraushaar's view is now almost generally accepted, and it is assumed that the hydration, not the oxidation, of CaS is the first process to be aimed at; dry CaS does not oxidise into polysulphide or thiosulphate, but into sulphite and sulphate. This matter has been further elucidated by Divers,[2] who had for the first time prepared pure calcium hydrosulphide, $Ca(SH)_2,6H_2O$, a salt which can only exist at common temperatures and in an atmosphere of

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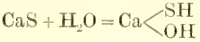
[1] We use this as the ordinary expression, although Divers has shown that it is only true in a limited sense.

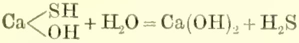
[2] S. C. I. 1884, p. 550; *cf.* also Divers and Shimidzu, C. J. 45, 270, and Divers, ibid. p. 696.

H_2S. It is exceedingly soluble in water, but the concentrated solution decomposes voluntarily, with evolution of H_2S, calcium hydroxyhydrosulphide, $Ca(SH)(OH),3H_2O$, being precipitated. This salt already observed by Berzelius in the shape of acicular crystals, is colourless and moderately soluble in water, but decomposes therewith very soon into insoluble $Ca(OH)_2$ and very soluble $Ca(SH)_2$. In a somewhat concentrated solution of $Ca(SH)_2$ it is insoluble, and is not decomposed therein. Lime unites with $Ca(SH)_2$ to form insoluble $Ca(SH)(OH)$. It loses H_2S on exposure to air and absorbs CO_2 and O, but the latter probably indirectly. It is formed by the union of H_2S and slaked lime, and undoubtedly also by the hydration of CaS, and is no doubt present in the spent lime of the coal-gas purifiers. This hydroxyhydrosulphide is the first product of the weathering of soda waste by the hydration of CaS, and is the source of the hydrosulphide found in the lixiviation waters; but the process of hydration is very slow. It is, however, greatly favoured by the heat produced in blowing air through the waste, when polysulphide and thiosulphate are formed by oxidation.

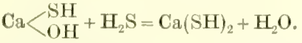
The stages of the process are thus:—

1. 

$$CaS + H_2O = Ca{<}\begin{matrix}SH\\OH\end{matrix}$$

2*a*. 

$$Ca{<}\begin{matrix}SH\\OH\end{matrix} + H_2O = Ca(OH)_2 + H_2S$$

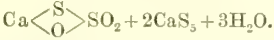
2*b*. 

$$Ca{<}\begin{matrix}SH\\OH\end{matrix} + H_2S = Ca(SH)_2 + H_2O.$$

It cannot be doubted that in moist alkali waste free calcium hydroxide and hydrogen sulphide exist at the same time, and these too are, indeed, the ultimate products of the hydrolysis of the calcium sulphide.

The H_2S, almost as fast as it forms, is oxidised by the atmospheric oxygen into H_2O and free sulphur, whilst (according to Divers) the calcium salts are not oxidised at all directly, nor does any appreciable quantity of H_2S pass into the state of SO_2. This free sulphur acts upon the calcium hydroxide in the way long known for the preparation of 'liver of sulphur,' viz. forming pentasulphide and thiosulphate thus:

3. $3Ca(OH)_2 + 12S =$



$$Ca{<}\begin{matrix}S\\O\end{matrix}{>}SO_2 + 2CaS_5 + 3H_2O.$$

The polysulphide is later on gradually oxidised into thiosulphate:

4. $CaS_5 + O_3 = CaS_2O_3 + S_3$.

In the presence of free lime the sulphur thus set free is again absorbed by reaction 3, so that more thiosulphate is formed, and by a succession of the reactions 3 and 4 ultimately the polysulphide is reduced to nothing. If, however, too little lime is present, free sulphur is left behind, and, if the contact with air is too extensive, H_2S will escape and lime will be left behind.

The just-mentioned ultimate conversion into calcium thiosulphate has been utilised for a long time past for the manufacture of thiosulphates (hyposulphites) from oxidised tank waste.[1]

Whatever may be the real theory of the 'weathering' of soda waste (to avoid the expression 'oxidation'), there is one obstacle to its practical utilisation—namely, that on the large scale it proceeds only to a certain stage, and then stops almost entirely, evidently owing to the fact that the new compounds formed protect the unchanged CaS from further action. This fact was recognised, and a remedy for it found about the same time by two observers, Schaffner and Mond, working without knowledge of one another. Schaffner first exposed the waste to the action of the air for about three weeks, then removed the soluble portion by lixiviation and repeated the weathering process several times, but after the first time by blowing chimney gases (containing CO_2 and O) through the mass. Mond's process is better adapted to the requirements of a large manufactory. He commences at once with blowing air through the waste by means of a Schiele's fan-blast, either in the lixiviation tanks themselves after removal of the proper tank liquor, or in special tanks provided with lixiviating apparatus. He thus arrives at the stage reached by Schaffner in three weeks, in about sixteen or eighteen hours, the heat evolved in the process immensely assisting the action. In both processes the oxidised waste is now lixiviated, first with weak liquor from a former operation, then with fresh water, and is then oxidised again by blowing air or chimney gases into it, to be followed by another lixiviation. Three successions of oxidation and lixiviation are the minimum, but as many as six double operations of this kind are required to extract about half of the sulphur in a soluble form.

Schaeppi (S. C. I. 1882, 482) has shown that it is best to lixiviate a long time; that hot water is far preferable to cold; that the solubility of the sulphides is limited, and the sp.gr. chiefly depends on the thiosulphate. At 10°Tw. the liquor is sure to be underblown, at 18–20° it is overblown. The liquor comes out best when kept as nearly as possible at 12°Tw. (measured hot). With overblown liquors the mass sets hard, and there is much loss of sulphur. Old waste, after oxidising and lixiviating five or six times, sets hard and solid, so that neither air nor water can easily penetrate it, and in this condition it may still contain from 6 to 12 p.c. sulphur as sulphide, if the fresh waste contained 18 p.c.

With fresh waste the loss of sulphur as CaS in the waste is less, but it is always appreciable, and there is a much larger loss in the shape of calcium sulphite and sulphate. But all of this is now present in such forms that the waste remaining after Schaffner's or Mond's treatment may be cast out anywhere, without causing any nuisance. It is, however, still troublesome on account of its bulk, and therefore causes not inconsiderable expense for its disposal. Many attempts have been made to utilise it as a cement, or otherwise, but without very much success.

The '*yellow liquors*' obtained in the lixiviating process contain the sulphur in different forms of combination, one of them, as sulphate, being useless, and three of them in an 'available' form—namely, as hydrosulphide, polysulphide, and thiosulphate. On addition of hydrochloric acid the two former must yield

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[1] *Cf.* also Veley, S. C. I. (Trans.) 1885, 478.

H_2S, the last SO_2, and the composition of the liquor is most favourable if the relation of H_2S to SO_2 is exactly $= 2:1$, in which case $2H_2O$ and 3S will be formed, and no sulphur will be lost. If, however, the sulphides are in excess, H_2S will escape, and, with an excess of thiosulphate, SO_2 will be formed. It is therefore necessary to manage the oxidising process so as to obtain the above proportion as nearly as possible, and Mond devised expeditious methods for carrying out the required testing of the liquor. Since over-oxidising does less harm than the reverse, the proportion is kept rather below $2H_2S$ to $1SO_2$.

The decomposition of the sulphur liquor was first carried out by Schaffner in a very ingenious but complicated way, and which he abandoned in favour of Mond's process, which consisted in simply mixing the sulphur liquor with a very slight excess of hydrochloric acid over and above that theoretically required, at a temperature of 60°C., with continuous agitation of the liquor. Below 40°C. much H_2S escapes, and the sulphur does not settle well. The reactions are:

$$Ca(SH)_2 + 2HCl = CaCl_2 + 2H_2S$$
$$CaS_5 + 2HCl = CaCl_2 + H_2S + S_4$$
$$CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S$$
$$2H_2S + SO_2 = 2H_2O + S_3.$$

By accessory reactions, small quantities of polythionic acids and calcium sulphate (apart from that owing to the sulphuric acid present in the hydrochloric acid) are formed, also a little hydrogen persulphide, which imparts a fœtid smell to the sulphur. It is decidedly necessary to perform the mixture of sulphur liquor and acid in such manner that the former at once meets with a quantity of acid sufficient for its total decomposition; otherwise H_2S is formed, and escapes as such. It is not possible to avoid the formation of some calcium sulphate, even when working with hydrochloric acid free from sulphuric acid.

The milky mass produced is separated by canvas filters into a solution of calcium chloride, containing small quantities of HCl and SO_2, which is run to waste, and a pasty mass, containing sulphur in an extremely fine state of division, mixed with a somewhat large quantity of calcium sulphate. This mass must first be freed from the adhering mother-liquor by washing, and must then be converted into pure sulphur by melting. The latter process is, however, very troublesome, since the heat penetrates very slowly into the porous mass. This difficulty was overcome by Schaffner, who performs the melting by steam of about 2½ atmospheres pressure, employing a double cylindrical vessel. The pasty mass is introduced into the inner cylinder, and the steam into the outer cylinder, communication being established only by means of an opening on the top of the inner cylinder, and the proper mixture of the mass with the steam entering here being brought about by an agitating shaft. This makes it impossible for the melted sulphur to be sucked back into the steam-pipe on any diminution of pressure in the steam-boiler.

Before starting the operation, some milk of lime is put in with the paste of sulphur and gypsum; this is done in order to convert the arsenic present (introduced by the hydrochloric acid employed) into calcium sulph-arsenite, and thus to keep it out of the sulphur. As the temperature exceeds the melting-point of sulphur, the latter collects in a perfectly pure state at the bottom of the inner cylinder, and can be tapped off there; whilst the gypsum is kept in suspension by the water present.

The recovered sulphur should be deprived of its unpleasant smell of hydrogen persulphide by melting it up in a cast-iron pot and blowing a strong current of air through it for some hours. This will also remove any traces of water, and will cause any ferrous sulphide present to settle out. After this treatment the recovered sulphur is cast into the ordinary stick moulds, and is not distinguishable by colour, density, or smell from refined Sicilian roll brimstone.

J. Robinson (Eng. Pat. 497, 1885) describes a special treatment for the removal of arsenic.

Chance (Journ. Soc. Arts, 1882, p. 726) quotes the following results obtained by the five British firms which carry out Mond's sulphur recovery process:—

No.	Recovered sulphur	Per cent. of total sulphur in waste	Hydrochloric acid consumed per ton of recovered sulphur
	tons		
1	6690	30	3·5
2	1500	27–30	4
3	3200	25–30	4 to 4·5
4	3000	?	4
5	3223	17	?
—	17613	—	—

P. W. Hofmann's process (patented in 1866) depends upon the hastening of the oxidation of soda waste by moistening it with 'still-liquor'—that is, the mixture of manganous, ferric, and hydrogen chloride formerly run to waste in the manufacture of chlorine. This process, which was practically carried out at the Dieuze works for a number of years, is extremely complicated, and must be considered obsolete now that at no alkali works is any still-liquor run to waste. We therefore simply refer to the descriptions of E. Kopp, in Wurtz's Dictionnaire de Chimie, 2, 1593; and publications in D. P. J. 191, 304 and 464; 192; 64 and 133.

Any process based upon the employment of hydrochloric acid must count with the fact that the value of this acid is continually rising in proportion as the price of Leblanc soda is lowered by the competition of the ammonia soda. Therefore special interest attaches to those processes which dispense with the use of hydrochloric acid for recovering sulphur from soda waste.

Mawdsley and Macfarlane (Eng. Pat. 11,178, 1885) treat 'yellow liquor' of 20°Tw. with ferrous chloride liquor (from copper-extracting works, &c.), whereby a black precipitate is formed, which is filtered, washed, and dried at a low heat. It is then heated in a muffle furnace, carefully protecting it from air, and the sulphur which volatilises is condensed as such. After this the heating is continued with access of air, so that the FeS remaining from the former operation is burned; the SO_2 is conducted into a vitriol chamber, and the ferric oxide can be used as a pigment. This process might be locally useful for disposing of two waste substances at the same time.

One of the most promising processes for recovering, not merely the sulphur, but even the lime contained in soda-waste, was that of Schaffner and Helbig (patented March 9, 1878). It aims at recovering the *whole* of the sulphur, and practically abolishing soda waste altogether. It is based on the property of magnesium chloride to decompose, at a boiling heat, the calcium sulphide, whilst calcium carbonate is not acted upon: $CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S$. This operation is performed in soda waste fresh from the lixiviating tanks, and hence not oxidised, and the hydrogen sulphide evolved is dealt with as will be described hereafter. The residue is now a solution of calcium chloride, holding in suspension a mixture of very light and finely-divided magnesia, with heavier and coarser particles of cinders, coke, limestone in excess, &c., and the latter can be mechanically separated from the former by passing the mixture through a sieve. The purified mixture of calcium-chloride solution and solid magnesia is now treated with more or less impure carbonic acid, from a limekiln, &c., and is decomposed into magnesium chloride and calcium carbonate:

$$MgO + CaCl_2 + CO_2 = MgCl_2 + CaCO_3.$$

The calcium carbonate is recovered by settling and washing, and can be used over again in the black-ash process; the magnesium chloride thus regenerated is concentrated by evaporation, and is used over again in the first stage of the sulphur-recovery process, as just described. The hydrogen sulphide evolved in the same stage is not, as was the case in all previous processes, diluted with a large quantity of inert gases, but is quite pure, and can be utilised, either by burning it altogether, and converting the SO_2 into sulphuric acid, or by taking away one-third of it, burning it into SO_2, mixing this with the remaining $2H_2S$, and thus obtaining all the sulphur: $2H_2S + SO_2 = 2H_2O + S_3$. This plan, so often unsuccessfully tried before, has been made practicable by Schaffner and Helbig, by bringing the gases in contact with one another in the presence of a solution of calcium chloride, which causes the sulphur to change from its milky, non-subsiding state into that of a flaky, readily-settling precipitate.

Stingl and Morawski (J. pr. [2] 20, 76) have minutely studied Schaffner and Helbig's process. They found that the formation of polythionic acids could not be prevented, but that it consumed only a few per cents. of the sulphur, and that it had nothing to do with the physical state of the sulphur precipitate, which is determined by the presence or absence of the calcium chloride solution. Debus (C. J. 1888, 278) has found that some of the sulphur is in actual solution in the colloidal state, and that this state is changed by the presence of saline solutions.

The sulphur thus obtained is washed, melted by steam in the Schaffner apparatus previously described, and thus converted into refined brimstone.

The Schaffner-Helbig process has been worked out on a practical scale by Al. M. Chance, who has described the apparatus and process employed at the Oldbury works in the Journ. Soc. Arts, 1882, 724, and in the S. C. I. 1882, 264; 1883, 202. By his endeavours it was proved that the process is perfectly practicable, except that he preferred to burn the H_2S for the manufacture of the sulphuric acid. The cost of recovering the sulphur amounted to 3*d*. per unit, and when the pyrites companies lowered their selling price to that figure the Schaffner-Helbig process had to be given up.

The most rational and obvious way of recovering the sulphur consists in treating the tank waste with carbonic acid (first attempted by Gossage in 1837), in order to recover also the lime as calcium carbonate. The hydrogen sulphide is utilised by burning it, and converting it into sulphuric acid, or else absorbing it by ferric hydrate, or in some other manner. But the following circumstance is a great drawback to this plan: the carbonic acid employed for this purpose must practically be the very impure gas evolved in limekilns or the like; hence all its impurities (especially a very large quantity of nitrogen) remain with the H_2S. The difficulty of disposing of the latter to advantage has, until quite recently, baffled the most persistent endeavours of Gossage himself and other inventors. Burning very dilute hydrogen sulphide is difficult, and certainly not profitable. It is much less difficult to burn the purer hydrogen sulphide, obtained in the saturation of the gases from ammoniacal gas-liquor, and this problem has been successfully carried out a number of years ago; but such, or even purer, H_2S is only obtained by the most recent processes for recovering sulphur from tank waste, to be described further on.

Attempts have also been made to burn H_2S in pyrites kilns, in contact with burning pyrites (Favre, in 1855; Kunheim); or to absorb the SO_2 formed in water, driving it off by heat, and passing it into an acid chamber (Gossage, in 1857), &c.

Claus (Eng. Pat. 4,922, 1886) burns H_2S into SO_2 and steam, and passes the mixture into a 'Hargreaves' apparatus, where it decomposes common salt into sodium sulphate and hydrochloric acid. The former is converted by the Leblanc process into soda, thus again yielding alkali waste; or the common salt is mixed with small coke, and the resulting mixture of coke and sodium sulphate is reduced by 'water gas' (that is, a mixture of carbon monoxide and hydrogen) to sulphide. The latter is, by the combined action of CO_2 and steam, converted into sodium carbonate and hydrogen sulphide, which is burned over again and used as before. The CO_2 is obtained by the gas resulting from the action of the water-gas on the sodium sulphide.

There is another way of burning H_2S, viz. employing only such a quantity of air that the hydrogen is burned but the sulphur is set free, and can be collected as such. After previous attempts in this direction had failed, Claus has solved the problem by passing the mixture of H_2S and air through red-hot ferric oxide, in the manner described in the art. Ammonia, vol. i. p. 100. This process has the great advantage of being applicable to H_2S, diluted with a large quantity of inert gas, such as would be formed by decomposing tank waste with impure CO_2;

and in Chance's process the H_2S is actually utilised in this manner, when not burned for the manufacture of sulphuric acid (*cf.* p. 493).

Miller equally employs air, but indirectly. He passes the hydrogen sulphide over red-hot calcium sulphate, which causes the formation of calcium sulphide, steam, and sulphur vapour (the latter being, of course, afterwards condensed): $CaSO_4 + 4H_2S = CaS + 4H_2O + S_4$. When most of the calcium sulphate has been reduced, it is regenerated by heating it in a current of air: $CaS + O_4 = CaSO_4$. This process would, however, seem to be much less simple than that of Claus.

A similar result, but in a different way, has been many times aimed at by bringing H_2S into contact with SO_2, either formed by burning part of the H_2S itself, or supplied in the shape of kiln gases. The principal reaction is

$$SO_2 + 2H_2S = 2H_2O + S_3;$$

but by a secondary reaction some pentathionic acid is formed:

$$5SO_2 + 5H_2S = S_5H_2O_6 + 4H_2O + S_5.$$

There is a loss of sulphur in this way, and much more is lost by the fact that the sulphur is in an extremely fine state of division, or even partly dissolved, according to Debus (see above), so that much of it runs to waste with the liquor. The latter difficulty has been overcome to some extent by Schaffner and Helbig's application of calcium chloride liquor (comp. above); but, in actual manufacturing, Chance was not able to work this process with sufficient ease. Kynaston (Eng. Pat. 2,473, 1885) appears to get better results in a different way, by the mediation of calcium sulphite; but as his process involves the use of hydrochloric acid, it is not economical. Parnell and Simpson (Eng. Pat. 14,364, 1885) bring SO_2 and H_2S into contact in the presence of dilute sulphuric acid, in which the polythionic acids accumulate, and are afterwards decomposed by heating the acid.

Many attempts have also been made to utilise the H_2S by absorbing it by ferric hydroxide or by ferric chloride

$$(Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S),$$

with regeneration of the oxide or chloride by blowing in air; or by employing it for precipitating copper and other metals from their solution, which, of course, is only practicable under exceptional conditions. Barrow (Eng. Pat. 17,528, 1888) describes special apparatus for this purpose.

Passing over the earlier attempts at decomposing tank waste by carbonic acid, to which Mr. Gossage unsuccessfully sacrificed thirty years of his life and a fortune, we shall describe the most recent and ultimately successful attempts in this way.

Opl's process (1882) originally consisted in exposing soda waste, suspended in three times its volume of water, to the action of CO_2, when calcium sulphydrate is formed:

$$2CaS + CO_2 + H_2O = CaCO_3 + Ca(SH)_2.$$

By employing more CO_2, the sulphydrate is decomposed into $CaCO_3$ and H_2S.

This process being incomplete, and requiring the use of pure CO_2, it was exchanged in 1883 by Opl and von Miller for the following process (Germ. Pat. 28,067). Soda waste, suspended in water, is treated with H_2S, when all the CaS is converted into a solution of $Ca(SH)_2$, which is separated from the insoluble portions of the waste. (Divers, *l.c.*, doubts the completeness of this reaction.) The solution is boiled, whereupon the H_2S is set free and lime is precipitated:

$$Ca(SH)_2 + 2H_2O = Ca(OH)_2 + 2H_2S.$$

Half of the H_2S is used for the first stage of the process ($CaS + H_2S = Ca(SH)_2$); the other half is utilised in one of the ways indicated above, or is burned for making sulphuric acid. The objections made to this process by Divers (*l.c.*) were controverted by Weldon (S. C. I. 1885, 171). This process was, however, tried on a large scale at the Rhenania Chemical Works, as minutely described by Hasenclever (Chem. Ind. 1889, 434) and Deutecom (*ibid.* 1890, 25), but it did not pay.

Lombard (Eng. Pat. 3,884, 1883) prepares a solution of $Ca(SH)_2$ in exactly the same way, and runs this into a solution of calcium phosphate in hydrochloric acid; bicalcium phosphate is precipitated, and H_2S is set free. (This process, in reality invented by Gladysz, is actually carried out in a factory in the South of France, but is evidently of very limited applicability; *cf.* also Simpson's process, *supra*, p. 456.)

Haddock and Leith (Eng. Pat. 11,296 and 15,648, 1890) treat a similar solution of calcium sulphydrate with a solution of sodium sulphate, separate the gypsum, carbonate the sodium sulphydrate solution, and employ the H_2S given off for treating fresh soda waste or milk of lime. This process is very similar to Simpson's second process, p. 456.

F. B. Rawes (Eng. Pat. 1,393, 1882) treats soda waste with a solution of sodium bicarbonate, and exposes it to a current of carbonic acid, with strong agitation, in order to expel the hydrogen sulphide. The bicarbonate was supposed to serve as carrier of CO_2 (which has since been proved to be quite erroneous). Laboratory experiments made by Kemp (S. C. I. 1885, 144) with this process yielded very good results, but cannot be accepted as valid for the large scale.

James Hargreaves, T. Robinson, and John Hargreaves (Eng. Pat. 1,371, 1888) describe mechanical means for promoting the decomposition of soda waste by CO_2.

The Chance-Claus process. The real solution of the problem of economically decomposing soda waste by carbonic acid was only achieved by Mr. Al. M. Chance in 1887 and 1888, partly by attention to all the details, and thus obtaining much more regular and rich mixtures of gases, partly by so manipulating the process that a quantity of nitrogen is got rid of, and this injurious ballast is lessened.[1] Thus, sulphuretted hydrogen is obtained of regular and constant composition, sufficiently rich to serve not only for the recovery of sulphur by the Claus kiln, but also for the successful manufacture of sulphuric acid. (The mediation of soda is not necessary for the process; indeed, Davidson and Davis (Eng. Pat. 8,901, 1891) actually destroy any sodium carbonate or sulphide present by addition of calcium chloride.) The process is carried out as follows:

Alkali waste, as fresh as possible from the tanks, is made into a thin cream with water, and the coarser particles are removed by a sieve.

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[1] Eng. Pat. 8,666 of 1887; S. C. I. 1888, 162.

The remaining portion is run into cylindrical vessels, 5 feet wide and 16 feet high, seven of which are combined into a set, furnished with inlets and outlets for gases, and such an arrangement of taps that the stream of gases can be manipulated in any desired way. Such a set suffices to treat the waste from 300 tons of sulphate of soda per week. Hargreaves, Robinson, and Hargreaves have taken out a patent, No. 6,968 of 1889, for an apparatus forming a combination of black ash lixiviating tanks and carbonators, both operations being carried out in the same vessels.

Carbonic acid from lime kilns, made in the best possible manner (in which case it will average about 28 p.c. CO_2 and 72 p.c. N), is pumped through those vessels. In contact with fresh soda waste, the CO_2 is absorbed by any free lime present, and by CaS, with production of $CaCO_3$ and H_2S. The latter being driven forward, passes into another vessel, where it meets a further quantity of alkali waste, and is absorbed, with production of sulphydrate, $Ca(SH)_2$. The gas issuing from here for a time contains only traces of CO_2 or H_2S; it is, in fact, almost pure nitrogen, and is allowed to escape, passing, as a precautionary measure, through a purifier containing oxide of iron or lime. Thus a considerable quantity of nitrogen is eliminated.

After a certain time, however, this process must be changed, for the CO_2 acts upon the $Ca(SH)_2$, and evolves H_2S:

$$CO_2 + Ca(SH)_2 + H_2O = CaCO_3 + 2H_2S.$$

When this begins to take place, the outlet from the last vessel is closed, and another outlet is opened from an intermediate vessel, from which H_2S is issuing in sufficient strength. This gas is conducted to a gasholder, till it ceases to be rich enough. When this takes place, the outlet is closed; the first vessel or vessels, in which the alkali waste had been entirely decomposed, having been emptied and refilled with fresh waste, the operations are resumed as at first.

There is thus a reversal of the operations from time to time. For an hour to an hour and three-quarters, nitrogen escapes into the air; then for $2\frac{1}{2}$ to $3\frac{3}{4}$ hours sulphuretted hydrogen of an average strength of about 32 p.c. passes into the gasholder; after this the first operation is resumed, and so on.

The waste is so completely decomposed that the filtered water does not blacken lead salts; it consists of carbonate of lime quite sufficiently pure for black-ash mixing, and is especially valuable for this purpose by containing $2\frac{1}{2}$ to 3 parts soda to every 100 parts of alkali produced. It seems, also, very well adapted for the manufacture of cement. Hargreaves, Robinson, and Hargreaves (Eng. Pat. 94, 1889) improve it for this purpose by a treatment with air or another oxidising agent in order to remove any residual calcium sulphide. The filtered water can be run to waste, or continually used over again.

The sulphuretted hydrogen is collected in a gasholder, 50 feet in diameter with a 17-feet lift, holding about 30,000 feet of gas; the water being covered with a layer of heavy coal-tar oil, no escape of H_2S takes place. This gas is now either utilised in a Claus kiln, where melted brimstone or flowers of sulphur are obtained, or else it is burned and vitriol is made of it. By having at command rich gases, of regular composition, this operation has been rendered perfectly successful. The heat generated is amply sufficient to work a Glover tower, and moreover to concentrate a considerable quantity of acid in a pan on the top of the kiln; the chamber space required is no larger than in working Spanish pyrites; the consumption of nitre is from 1·15 to 1·44 p.c. on the dry SO_3 produced. The vitriol produced accounts for 98 to 99 p.c. of the H_2S as drawn from the gasholder, and for 95 p.c. of the sulphur contained in the waste, a few per cents. of sulphur being lost in the shape of FeS and in the oxide purifier. The vitriol is quite free from arsenic, contains a mere trace of iron, and is almost colourless. The labour is less than that for breaking pyrites and working the kilns, and apart from the steam for pumping CO_2 no fuel is used.

Experience has shown that the manufacture of sulphuric acid from the sulphuretted hydrogen made by the Chance process cannot compete with that from pyrites, if the sulphur in the latter costs less than 3*d.* per unit (which has been the case during the last few years). It is, therefore, generally preferred to treat the H_2S by the Claus process (*cf.* p. 491). It is mixed with a quantity of air corresponding as exactly as possible to the proportion $H_2S + O$ (4 vols. of air to 5 vols. of 33 per cent. H_2S); the mixture is passed from the top downwards through iron cylinders, lined with fire bricks, in which an 18-inch layer of ferric oxide is contained on a grate, and kept hot by the heat generated in the process itself. Here the reaction

$$H_2S + O = H_2O + S$$

takes place, both the products of it being necessarily in the state of vapour. The mixture of steam and sulphur vapour is first carried through a chamber, formed by a cast-iron pan arched over, where much of the sulphur condenses in the liquid form, and is twice a day tapped off at the bottom. The vapours then pass into a large brick chamber, where the remainder of the sulphur is condensed in the shape of 'flowers of sulphur'; last of all, the steam is condensed as water. The gases issuing from this chamber still contain some unburnt H_2S, as well as some SO_2; they are very difficult to treat, and are mostly burnt in order to convert the H_2S into the less objectionable form of SO_2, which can be, at least to a great extent, removed by washing with water. Other means of dealing with the H_2S, *e.g.* passing the gases through milk of lime, have been found too expensive. It is to be hoped that this drawback will be overcome, as it causes a somewhat considerable loss of sulphur, and the large escape of SO_2 is certainly not to be neglected as a nuisance. The much greater nuisance at first caused by accidental escapes of sulphuretted hydrogen through leaking joints, taps, &c., seems to have been greatly lessened by the further experience gained in the working of the Chance process. But it has been found out that sulphuretted hydrogen acts more strongly upon iron than it had been suspected, and costly repairs are hence unavoidable.

Hargreaves (Eng. Pat. 10,322, 1888) replaces the ferric oxide in the Claus kilns by perforated blocks of earthenware or metal, for which very ingenious mechanical arrangements are described.

Decomposing soda waste by superheated steam was tried by Grouven (Germ. Pat. 29,848) in a special manner. The waste is mixed with some sawdust and water, moulded into the shape of drain-pipes, exposed to the air for two days, and put into retorts, where it is treated with superheated steam. The carbonaceous matter present reduces all the oxidised sulphur compounds to calcium sulphide, and this itself is, at a high temperature, decomposed by superheated steam into calcium oxide and hydrogen sulphide.

Treatment of the drainage from old tank waste heaps.—This drainage was deodorised at South Shields, on the author's plan, by mixing it with the mud from the manganese liquor settlers of the Weldon process, consisting chiefly of ferric hydroxide and calcium carbonate and sulphate, with a little manganese peroxide and manganous chloride. The ferrous and manganous sulphide thus formed were revivified by exposing them to the air; and this, according to R. Angus Smith, can be made a continuous process by blowing air through the liquid.[1] The formation of a considerable quantity of thiosulphate, apart from other difficulties to be removed by further efforts, render this process not sufficiently profitable. The process as carried out at South Shields certainly removes the nuisance caused by the drainage.[2]

By another process, patented in 1871 and 1878 by Mactear, the drainage of the immense tank waste heap accumulated at St. Rollox, amounting to 13,000 gallons per day, is profitably worked for sulphur. These yellow liquors contain far too much sulphide in proportion to thiosulphate, so that on adding acid the reaction $2H_2S + SO_2 = 2H_2O + S_3$ is not brought about completely, very much H_2S being given off. This is corrected by adding to the liquor sulphurous acid, in one shape or another, till the proper composition is attained. The sulphurous acid is obtained by passing the fumes of burning sulphur or pyrites-kiln gases through a wooden coke tower, fed with water; or calcium bisulphite is made in a similar manner, and is added to the yellow liquor in sufficient quantity. Thirty tons of sulphur per week are produced in this way, at a cost of 61*s.* per ton, calculated indirectly, and without allowing anything for the value of the hydrochloric acid.

The same object is attained in a simpler and cheaper form by Péchiney. He blows air through the tank-heap drainage liquors till the oxidation has reached the proper degree. In doing this, about one-fourth of the lime is precipitated (a reaction explained by Divers, *l.c.*), and thus a corresponding quantity of hydrochloric acid is saved in decomposing the oxidised liquor.

THE MANUFACTURE OF SODA BY THE AMMONIA PROCESS.

The first germ of this process, which has quite revolutionised the alkali trade, is, as usual, found to have sprung up in various quarters.[3] A German chemist, Vogel, is said to have known the reaction as early as 1822, and a Scotch chemist, John Thom, seems to have actually made some soda, in a crude way, by that process in 1836. Mond has definitively disposed of the attempt made by several French *savants* to claim the merit of the invention of this process for their countrymen, Schloesing and Rolland. Quite recently a claim has been set up for Fresnel, who is said to have made soda from common salt and ammonium carbonate in 1811, according to some hints found in recently-discovered private letters; evidently he did not meet with much success, as nothing came of his attempts. It is beyond doubt that the real history of the ammonia process dates from June 30, 1838, on which day Harrison Grey Dyar and John Hemming, both chemists residing in London, patented a process embodying all the principal reactions now carried out. This was done even more clearly in an additional patent, taken out in France on May 18, 1840, on their behalf, by Delaunay, where the use of a current of carbonic acid is first mentioned. A number of patents by other inventors followed, among which that of Gossage (1852) is remarkable, and those of Schloesing and Rolland (1854 and 1858) have become best known by the detailed description they gave in 1868 of their process.[1] Although their apparatus was very ingenious, it must have been deficient in important portions, for they could not make their works pay, and the reasons given for their abandoning the process are quite inconclusive.

In many other places works had been erected for making ammonia soda: by Dyar and Hemming, in Whitechapel; by Muspratt, at Newton; by Gossage and Deacon, at Widnes; and by a number of French and German manufacturers. But although we find every feature of the now successful processes in these older establishments, there was always something or other wanting, and especially the loss of ammonia seems to have been too great, so that at that time the ammonia soda could not compete with the Leblanc soda even in localities where the loss of the hydrochloric acid would not have been of much consequence at that time. Apparently, about 1860, nobody manufactured ammonia soda, and the failure of all previous attempts in that direction had evidently discouraged nearly all chemists.

It was reserved to Ernest Solvay, of Brussels, to find the solution of that long-pursued problem. His first patent dates from 1861, but the process as we know it now is first described in his English patent of September 12, 1863, followed by many others in 1872, 1876, 1879, and later on. His works at Couillet, in Belgium, were started in 1863, and soda made there was exhibited in Paris in 1867 without exciting much attention. But since 1872 his triumph was assured, and has given rise to a host of other inventions, most of which have again passed into oblivion, while a few have stood the test of practice; so that ammonia soda is now manufactured not merely by Solvay's processes (which certainly furnish the largest share), but by several other independent and partly secret processes.

We mention of other recent processes than Solvay's those of Honigmann (Lunge's Alkali,

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[1] Report on the Alkali Act, 1877-78, pp. 9 and 29 *seq.*

[2] Dr. Ballard's Report to the Local Government Board for 1878, p. 225.

[3] Compare, on the history of this process especially, Mond, S. C. I. 1885, 527, and Scheurer-Kestner, *ibid.* 1886, 322 (from Bl. 45, 302).

[1] A. Ch. 64, 1.

iii. p. 36), Pollacsek (*ibid.* p. 37), J. Young (1872), Hugo Müller (1874), Gerlach (D. P. J. 223, 82), Wallace and Claus (1877), Unger (1877), Verzijl (1876), Boulouvard (1872 and 1877), Count Montblanc and Le Gaulard (1879), Bernard (1877), Scherbascheff (1876), Thowald Schmidt (C. N. vols. 34, 37, 38), Grousilliers (1875), Ortlieb and Müller (1880), Maguin (1883), Wigg (1882, 1884, 1885, 1888), Schaffner and Helbig (1881), Parnell and Simpson (1885), Schloesing (1878–85), Strassburger and Frauenkron (1884), Pick (1885 and 1886), Claus, Sulman, and Berry (1889), Staub (1888), Wood (1888), Davis (1888).

The theory of the ammonia soda process is very simple, and is expressed by the equations

(1) $NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl$;

(2) $2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$;

that is, sodium chloride is treated with ammonium bicarbonate, either directly or indirectly, in successive stages—namely, first by ammonia and then by carbonic acid. If this treatment takes place at a low temperature, it leads to the precipitation of sodium bicarbonate, this salt being difficultly soluble in a solution of ammonium chloride. From sodium bicarbonate the normal carbonate can be obtained by heating. The mother-liquor, containing ammonium chloride, is treated with caustic lime, and the ammonia is thus recovered, calcium chloride remaining behind as a waste, but inoffensive, product.

Several chemists have made laboratory investigations of the ammonia-soda process. Heeren (D. P. J. 149, 47) showed that the decomposition, as indicated by the above equation (1), is not complete. Even by an excess of ammonia and carbon dioxide only two-thirds of the sodium chloride is decomposed. Bauer (B. 7, 272) showed that the incompleteness of the reaction is not merely due to the solubility of sodium bicarbonate in the mother liquor, but to the fact that the inverse reaction—that is, the conversion of a mixture of sodium bicarbonate and ammonium chloride into ammonium bicarbonate—takes place to some extent whichever way the conditions may be varied, even at −15°C. The same was noticed by Günsburg (B. 7, 644). He found that at 17°C. 100 parts of a saturated solution of ammonium chloride, containing 25·89 NH_4Cl, keep 5·742 $NaHCO_3$ in solution, and that quantity must needs be lost.

Honigmann (Hofmann's Bericht über die Fortschritte der chemischen Industrie, i. 452) found that of 100 NaCl 60 were recoverable as $NaHCO_3$, if the proportions are 1NaCl to $1NH_3$, or 66 parts with the proportions 4NaCl to $3NH_3$. In the first case each 100 parts of NH_3 precipitated 90, in the second case 101 parts NaCl.

Schreib (Z. f. angew. Chem. 1888, 283) has also found that the decomposition of common salt is always very incomplete.

In practice this incompleteness of the theoretical decomposition leads to a considerable loss of sodium chloride, for any bicarbonate left in the liquor, together with ammonium chloride, is at the subsequent heating of the liquor converted into sodium chloride by the reaction:

(3) $NaHCO_3 + NH_4Cl = NaCl + NH_3 + CO_2 + H_2O$

which at a higher temperature is complete. The NaCl remains with the calcium chloride liquor, and rarely pays the expense of recovering it.

Practically the manufacture of ammonia soda requires much more sodium chloride than that of Leblanc soda, and it is therefore most remunerative where common salt is extremely cheap, as at sea-salt works, or even more so in the form of strong brine as found in Cheshire, at Varangéville, in the east of France, and in many other places. The cost of the salt in the latter case is entirely nominal, and thus this item counts for much less than the smaller quantity of solid salt required for the Leblanc process. The pyrites and nitre required for the latter are entirely saved, and the consumption of coals in the ammonia process is always much below that required for Leblanc ash.

The only item of cost peculiar to the ammonia process is that for the unavoidable loss of the reagent ammonia itself. 100 parts of pure sodium carbonate are equivalent to 32·8 of ammonia, or 162·25 of ammonium sulphate; but in reality, as only two-thirds of the sodium is converted into carbonate, we must increase those figures to about 50 parts NH_3, or 250 ammonium sulphate, for each 100 parts of Na_2CO_3. $2\frac{1}{2}$ tons of ammonium sulphate cost about 30*l.*, 1 ton of pure carbonate of soda about 8*l.* It is, therefore, evident that the success of the process depends entirely upon so constructing the apparatus that all parts of it are air-tight, as a condition for the practically complete recovery of the ammonia from the ammonium chloride, and it becomes intelligible why, although all chemical conditions were perfectly understood before, it was reserved for the excellent mechanical contrivances of Solvay to overcome all the difficulties. With the most perfect apparatus, and with extremely careful work, it seems possible to recover 99 p.c. of the ammonia circulating in the system, leaving a loss of 2·5 ammonium sulphate to 100 sodium carbonate, but probably the loss is somewhat larger at the majority of works—viz. 4 or up to 8 parts of ammonium sulphate.

Apart from the advantages mentioned before, the ammonia process has several others over the Leblanc process. In the first instance it yields much purer sodium carbonate than the older process was formerly able to supply, both with respect to the percentage of available soda and the freedom from caustic soda, iron, and other objectionable impurities. Indeed, an article containing 98 p.c. of Na_2CO_3 (the remainder being chiefly NaCl) is regularly turned out here. Some of the best managed Leblanc works have within the last years come up to the same degree of purity, but they are exceptions, and even they can only supply part of their make in this shape, another part being always of poorer quality.

An extremely important advantage of the new over the old process is its freedom from any of the various forms of nuisance produced by the Leblanc process in its entirety, but most conspicuously by the tank waste. Indeed, if it were proved definitively possible to do away with the nuisance caused by the tank waste and at the same time to turn it to practical use by taking out the sulphur in a complete and cheap way, the Leblanc process would undoubtedly hold its own against the ammonia process, at any rate for a considerable time, unless, on the other hand, the efforts for recovering the chlorine from the mother-liquors of the ammonia process should prove successful, which as yet has certainly not been achieved (*v.* CHLORINE).

Nearly all the drawbacks formerly found in the ammonia process have now vanished, and only two remain, one of them certainly of the first importance. It is true that the manufacture of caustic soda is cheaper with the tank liquors from Leblanc soda than with ammonia soda dissolved on purpose. On the other hand, the latter yields caustic of extremely high strength and purity (compare above), and its inferiority in this direction is, therefore, not so great as was formerly assumed, and might easily be much more than counterbalanced by other advantages. But there remains a fundamental inferiority of the ammonia in comparison with the Leblanc process—viz. the fact that it yields the chlorine in a form as passive as that of the starting material, sodium chloride. The Leblanc process operates with a substance of great chemical energy—viz. sulphur in the shape of brimstone or pyrites—which is certainly converted into a much less active form, namely, calcium sulphide; but the very fact that this substance is a nuisance proves that the sulphur in it is still in an available form, and the question of recovering it by a *cheap* process seems now at last to have been solved by Chance's process. On the other hand, the Leblanc process furnishes the chlorine in the very active form of hydrochloric acid, which has many uses of its own, and which is easily convertible into free chlorine by atmospheric oxygen, with or without the intervention of manganese peroxide.

It is very different with the ammonia process. In this the converting agent, ammonia, is easily and almost completely recovered; but, just owing to the simple character of the fundamental reaction, the chlorine passes merely into the state of calcium chloride, in which it is practically useless. It is true that even from calcium chloride it is possible to prepare hydrochloric acid or chlorine, as we shall see, but this involves a considerable expense, and hitherto it has not been found economical. If the Weldon-Péchiney process for preparing chlorine from magnesium chloride (*v.* CHLORINE) should be proved to be as cheap as is at present affirmed, it would undoubtedly be applied to the ammonia-soda process as well, and would remove its inferiority in that respect; but the hopes held out a few years ago in that respect have not been realised.

Description of apparatus and processes for the manufacture of ammonia-soda.

Although Solvay's apparatus is only one of very many forms in which ammonia-soda can be made, we shall describe it more particularly, because it is undoubtedly the most successful in its way, and is, at the same time, better known than any of the other actually working processes. It is practically carried out at the numerous works erected by MM. Solvay and their partners in Belgium, France, Germany, Russia, America, &c., and at the large English works of Messrs. Brunner, Mond, and Co. The following description cannot, of course, contain the most recent improvements, as these are kept secret by the factories. We shall add to it, in the proper places, some notes on another successful plant as constructed by Boulouvard in the South of France.

1. *Preparation of the ammoniacal solution of sodium chloride.* Solvay has patented an apparatus for starting with solid salt, but practically he only employs brine, such as it occurs naturally or is artificially produced in Cheshire and elsewhere. This brine is not always sufficiently saturated, and it is always contaminated with magnesium and calcium salts, which must be removed. This can be done by various processes; for instance, by first precipitating the magnesia by milk of lime, and afterwards the lime by ammonium carbonate (a trace of magnesium carbonate always remains with the liquor). This purification can be effected in the same apparatus in which the brine is saturated with common salt and with ammonia, and the precipitate formed is removed by an automically-acting decanter. According to a patent of 1879, Solvay now seems to purify the brine previously to saturating it, by adding to it, while hot, sodium carbonate, together with a little chloride of lime, till all magnesia, lime, and ferric oxide are precipitated.

The apparatus for saturating the brine with ammonia is shown in fig. 42. R and R′ are tanks for brine; A is the dissolver for ammonia, communicating with R and R′ above and below by the cocks r^1 and r^2; only one of the tanks, R R′, alternately, is connected with A. Suppose this to be R, r^1 and r^2 are opened, and ammonia-gas, together with some CO_2, is admitted through the pipe T, coming from the still into A, where it is distributed by the perforated false bottom F and quickly absorbed by the solution. From R, into which a suitable quantity of lime has been introduced, and the contents of which are agitated by W W′, the brine flows into A and back again; in case of need the circulation is promoted by a propelling screw, interposed in one of the connecting pipes. The cooling worm S, through which water is kept flowing, takes away the heat generated in A by the absorbing process. The pipe V serves for introducing ground salt, by means of a wheel *m* divided into several compartments, in case the brine is not strong enough. The air escaping through T′ is passed through an apparatus, where the ammonia which it contains is kept back.

The saturation of brine with ammonia must be carried to a certain point, and in this process the bulk of the liquid is very much increased. This increase has been utilised by Solvay in various very ingenious ways for automatically regulating the saturation, but this does not seem to be very essential, as the proper point can be, and always is, ascertained by titrating the ammoniacal brine.

A further indication is furnished by the specific gravity of the liquor, which before the ammoniacal treatment is = 24°Baumé, or 1·1956, and after that treatment = 16°Baumé, or 1·1246.

When the brine contains enough ammonia, the agitator in R is stopped and A is connected with R′. Most of the mud originally contained in the brine, and freshly produced by the precipitation of magnesia and calcium carbonate, settles down very quickly, and is drawn off by the bottom valves. The remainder is removed by the continuous decanting apparatus D. The mixture of mud and liquor is forced by carbonic acid, acting upon the surface of the liquid in R, through the pipe L, into the cylinder D. The liquid portion overflows at U; the mud settles down in the conical part, is scraped off the bottom by the scraper M, rises in the pipe J, and is run off through *t*. According to requirements, more or less of the contents of R are passed through D in this manner.

The liquor must now be completely freed from suspended particles by filtering through closely-woven cloth under strong pressure. This is done in the cylinder B, within which a smaller cylinder O, with many perforations, is fixed. The filtering-bag is either inside O, and consequently taken out when full of mud, or it is outside, in which case the mud is removed by *d*.

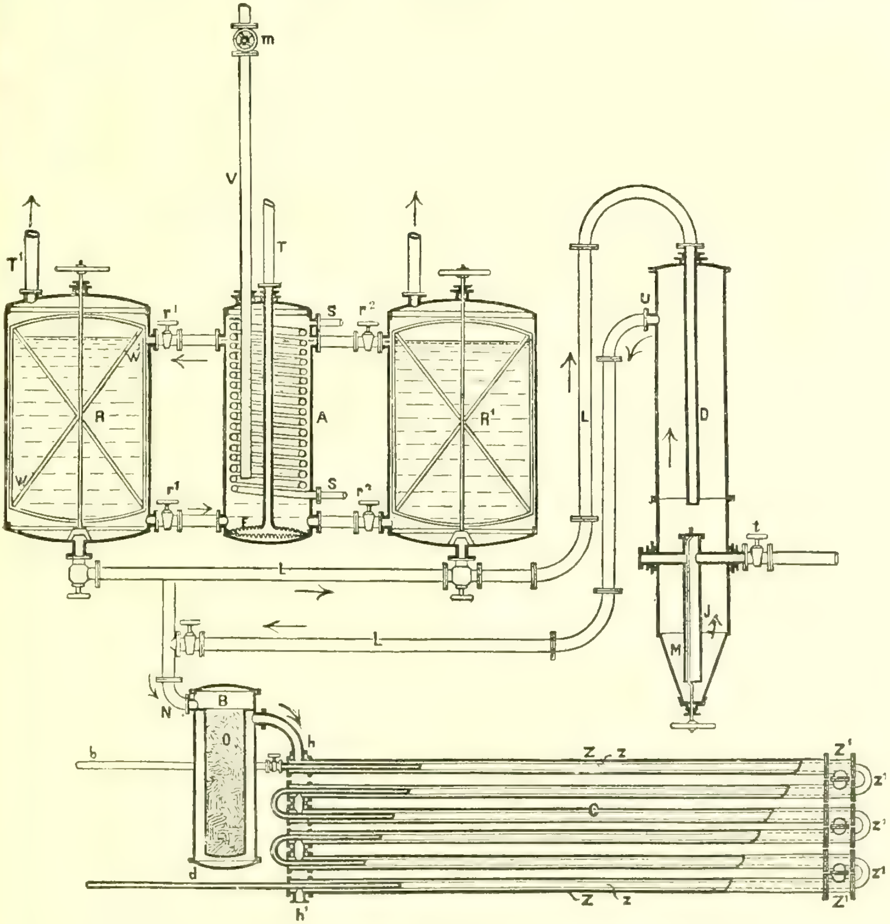

FIG. 42.

The clear ammoniacal brine must be cooled down further before being treated with carbonic acid. This is done in the apparatus C, composed of concentric tubes Z Z, like a Liebig's cooler. The inner tubes communicate alternately at their ends by bends Z′, and the outer pipes by the junctions shown in the diagram. The brine is run in the annular space between the two tubes, entering through h and leaving at h'. Cooling water is run both through the central tube and outside all over the apparatus.

The liquid is forced through the cooling apparatus, and on to the top of the carbonating columns, by means of carbonic acid coming from the large force-pump to be mentioned afterwards. The regulation is automatically performed by the apparatus, fig. 43. The liquid flows through the valve-box *c* into the vessel R; within this the float F rises until it touches the washer *r* fixed upon the rod *t*, which it raises, and with it the valve *s*, by which the opening s^1 is closed. *t* also acts upon the lever L, which raises the valve s^2 and admits into the apparatus compressed air or gas, which forces out the liquid through the valve-box c^1. The float F descends with the liquid till it comes into contact with the washer r^1, whereupon it draws down the rod *t*, which closes the admission of compressed gas and opens the valve *s* for the escape of compressed gas through s^1. Fresh liquid then enters through *c*, and the operation begins over again. An ordinary dial arrangement, applied to the lever L, indicates the number of times it has worked, and with it the volume of the liquid forced.

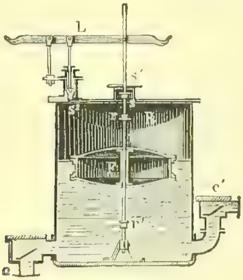

FIG. 43.

A patent of 1879 describes another arrangement, namely larger vessels, of which the first serves for the saturation itself, the ammonia gas meeting a continuous stream of brine. The latter, becoming turbid in this action, flows over into a second large tank, where the mud settles down. The clear liquor flows over into a third tank, by means of a pipe reaching to its bottom and perforated all along, thus becoming intimately mixed with the liquor already contained in that tank, and producing a mixture of uniform percentage of ammonia. By adding some sodium-carbonate in excess the remaining magnesia is precipitated.

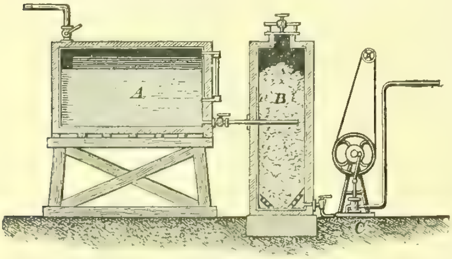

FIG. 44.

One of the few processes which have been successfully set to work, apart from Solvay's, is that of Boulouvard, and we shall describe this also, mainly because it starts from a different basis, namely from solid salt, which, when obtained as pure rock salt or sea salt, is sufficiently cheap for the ammonia process. It has this advantage in comparison with brine—that it does not require any preliminary purification from calcium and magnesium salts, and that it is not necessary in this case to obtain almost anhydrous ammonia, the salt being, on the contrary, dissolved in somewhat diluted liquor ammonia, as obtained in the recovery process (a principle already indicated by Heeren).

Boulouvard's apparatus for obtaining ammoniacal brine is shown in fig. 44. A is a lead-lined tank, containing ammoniacal liquor, which is diluted to the required extent and is then run into the box B, filled with salt. Here it dissolves salt, with absorption of heat, and passes through the filtering-bottoms *c c* to the pump C, in order to be continuously charged into the carbonator. Several such boxes work at the same time, so that the salt in those which have been partially emptied can be filled up again.

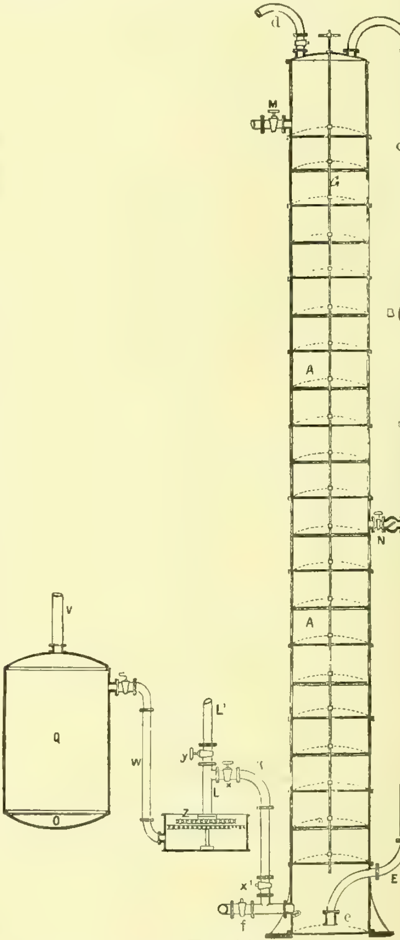

FIG. 45.

The saturation of the ammoniacal brine with carbonic acid is, perhaps, that part of the process which is of the greatest importance in the ammonia-soda method. Here the principal reaction takes place, and, since this belongs to the class of reciprocal reactions, as we have seen above, the best conditions must be obtained for making it as complete as possible in the sense wished for. Undoubtedly it is much more important, in every practical case, to prevent any loss of ammonia than to save more or less sodium chloride, and the work is from the first laid out with this view. The temperature is throughout kept down, because the conversion of NaCl into $NaHCO_3$ is favoured by low temperature and high pressure, the opposite reaction by high temperature and low pressure. The best temperature is considered to be at 15°C., but it is asserted that 30°C. may be attained without doing much harm. But since the reaction produces heat, such a temperature can be only attained by providing an efficient cooling system. The operation ought to go on quickly, both in order to get as much work as possible from the apparatus, and to avoid loss of ammonia by prolonging the time of working. The bicarbonate of soda ought to be precipitated in a state in which it can be easily separated from the mother-liquor, and the ammonia compounds washed out of it; and this is only possible if no bicarbonate of ammonia is precipitated together with the sodium salt.

Solvay's carbonating apparatus seems to fulfil all the necessary conditions, for it has been working now for many years without essential modifications, and has apparently been introduced in all the works erected under his patents. It consists of a cylindrical tower A A (fig. 45), composed of from 15 to 25 superposed cylinders of 3 feet 3 inches in height each, and of about twice that width. Each cylinder is fitted with a straight diaphragm, provided with a large hole in the centre, and above this with a plate of the shape of a spherical segment, perforated with a number of fine holes, and nicked round the edge (fig. 46). The guide-rod G allows some play to the plates. A better arrangement of guide-rods is shown in fig. 47, where *c* signifies the straight, *b* the spherical, diaphragm, and G the guide-rods.

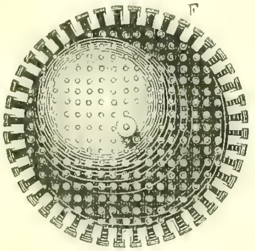

Fig. 46.

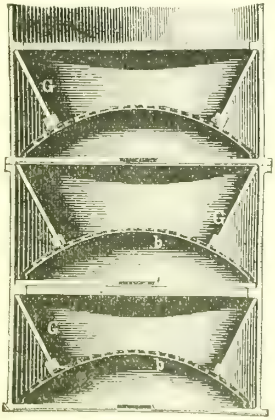

Fig. 47.

Carbonic acid (mixed with nitrogen, &c., as described below) is forced in at the bottom through pipe E by means of a blowing-engine, and the gaseous current is divided into many jets by the sieve *e*. As it rises up in a volume of liquor at least 40 feet high, it is not merely brought into intimate contact with the liquor (very much assisted by the large number of double perforated partitions), but, as it must expand from its original pressure of several atmospheres to that of the outer air, and in doing so performs a considerable amount of mechanical work, much heat is absorbed and the temperature is kept down.

It seems usual now to introduce another current of carbonic acid higher up in the tower, and to employ the richer gas for the lower, the poorer for the higher part of the tower, with a view of saturating the liquor with strong gas, before it is run off at the bottom, while weak gas is good enough to act upon the fresh ammoniacal brine higher up.

The gas escaping at the top at *d* (which gas still contains a somewhat considerable proportion of CO_2 and always carries away some ammonia) is first washed by a solution of salt, and then again by sulphuric acid, in order to retain all the ammonia. This may be done by means of coke-towers.

The *carbonic acid* is taken partly from the calcination of the sodium bicarbonate and partly from the lime-kiln, where the lime is burned for decomposing the ammonium-chloride liquor. Theoretically the former of these sources ought to supply half the CO_2 required, but it is very far indeed from that; for the full amount of CO_2 given off in calcining cannot be recovered, and nothing like the total amount of CO_2 introduced is utilised in the tower. Probably at least half as much again must be employed over and above the theoretical quantity.

The CO_2 from calcining the bicarbonate should be very pure if this operation is performed in close vessels, but it is otherwise where furnaces are used for this purpose. The gases from lime-kilns contain at the very best only 30 p.c.—often only 25 p.c.—by volume of CO_2. The richer the gas, the better it is for the process, and at some of the factories special means are employed to attain this end.

Several processes have been proposed for obtaining gas very rich in carbonic acid. Ozouf employs an apparatus in which the dilute gas is brought in contact with a solution of normal sodium carbonate; the solution of bicarbonate thus obtained is heated, whereby CO_2 is expelled and the original solution is recovered. Others decompose calcium carbonate in retorts kept at a red heat by means of superheated steam.

As far as it is known, all these proposals are too expensive, and the CO_2 is still everywhere obtained from lime-kiln gases, apart from that given off in calcining the bicarbonate.

Whichever source the carbonic acid is taken from, it must be thoroughly washed in order to remove any flue-dust and sulphur acids (from the coke), and it is thus cooled at the same time. While passing through the blowing-engines the gas becomes heated again to a considerable extent by the compression, and this heat must be removed by another washing with cold water before employing it in the saturating towers. This compressed and cooled carbonic acid also serves for propelling the liquor through the various parts of the apparatus, and any absorption of it taking place in this way is favourable to the process.

Returning to the carbonating tower, fig. 45, we notice the pipe *b*, through which ammoniacal brine is supplied to the apparatus from a main pipe B, so placed that the tower is always kept full to within 10 feet of its top. The liquor is introduced into the tower by a tap N, fitted with a valve, which opens towards the tower and prevents the liquor from running out in case of a stoppage. The main pipe B communicates with the top of the tower by the pipe *c*. The liquor thus passes first into the tower about the middle of its height, and the layer above this point to the top remains almost stationary, and is only gradually mixed with that below.

The object of this arrangement is the following:—The current of gases is very apt to carry away much free ammonia, but much less ammonia in the state of carbonate. If the liquor saturated with free ammonia entered at the top, it would lose very much of its ammonia in descending towards the bottom. But entering where it does, the upper portion of the column of liquor receives so much CO_2 before the ammonia can be carried away at the top that this loss is, for the most part, prevented. As the liquor gradually sinks down it becomes completely saturated with CO_2, and the precipitation of sodium bicarbonate takes place. The holes in the curved diaphragms would be soon stopped up with the precipitate, but this is to a great extent prevented by the shape of those plates, which causes the salt to slide down the marginal nicks and through the large holes of the straight diaphragms; also by introducing the gas not in a continuous jet, but in distinct puffs, which jerk the salt out of the holes. Still, these plates do get stopped up pretty often, and when this has taken place to an inconvenient extent the liquor must be run off and the salt dissolved by steaming out the tower, after which it must stand some time to be cooled; or else hot water is run in through tap M and run out at *f*.

The carbonating towers are continuously cooled from the outside by a copious stream of water. The heat is much more easily kept down if the first absorption of CO_2 by NH_3 takes place outside the tower, as there is nothing like as much heat cooled in the formation of bicarbonate from the normal carbonate. Therefore the saturation of the NH_3 with CO_2 is as much as possible effected beforehand, and the liquor properly cooled before entering the tower. Cogswell (Germ. Pat. 41,989) proposes a special system of cooling-pipes within the tower, and this seems to have answered very well.

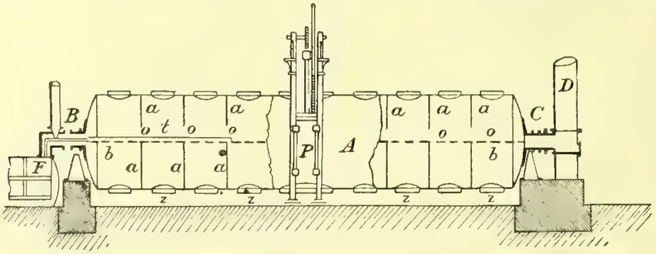

FIG. 48.

In certain intervals—say, every half-hour—the tap X′ is opened and a certain portion of the pasty mass contained in the carbonating tower flows through pipe K, tap *x*, and pipe L into the vacuum filter Z, consisting of a cylinder, 5 feet deep and 10 feet wide, with a perforated false bottom, covered with a linen or woollen fabric. The mass is evenly spread on the filter by issuing from the lateral openings of the supply-pipe, which is thereby caused to revolve round its axis. The space below the false bottom communicates by pipe W with a reservoir Q, in which a vacuum is produced by the pipe V, leading to an air-pump not shown in the diagram. The mother-liquor is thus drawn into Q, crystalline sodium bicarbonate remaining on the filter. Pipe L′ is arranged for sprinkling water on the salt (for which purpose tap *y* is opened and *x* and *x*′ are shut), or even for introducing hot air to dry the salt on the filter itself (which does not seem to be practically done). The water used for washing the bicarbonate is drawn off by the vacuum, and the washing process is repeated till the ammonia has been as much as possible removed. This is not possible without dissolving some of the sodium bicarbonate as well, nor is it possible to free this absolutely from ammonium compounds. The mother-liquor contains most of the ammonia as chloride, some as carbonate, together with a considerable quantity of sodium chloride and bicarbonate.

Solvay has further patented a somewhat complicated continuous revolving filter, which does not seem to be in practical use.

In 1879 he patented another continuous-washing apparatus, consisting of a long trough containing two longitudinal shafts revolving in opposite directions, and each provided with a worm, by which the salt is carried in one direction and the washing water in the opposite one, or else a series of small troughs, provided with small scrapers, and fulfilling the same purpose.

Boulouvard's carbonating apparatus, as first constructed and successfully worked, consisted of a series of ten cylinders, placed each a little higher than the preceding one, and fitted inside with revolving troughs. The ammoniacal brine passes from the top cylinders downwards, and the carbonic acid travels the opposite way. We show here a modification of this apparatus, as patented by Péchiney in 1880. Figs. 48 and 49 show a large cylinder A, revolving round its axle. It is provided with a perforated horizontal diaphragm *b*, running all its length, and with a number of perpendicular diaphragms *a a*, with central openings *o o* and manholes *z z*. Through one of the hollow trunnions, c, the ammoniacal brine enters and the waste gases escape. The inner tube *g* of the other trunnion B (shown in fig. 50), is longitudinally divided into two parts, each of which can be made to communicate by *i* with the downward branch *j*. This tube *g* serves for running out the mixture of liquor and suspended bicarbonate, and for introducing strong carbonic acid, obtained by calcining the bicarbonate, while impure carbonic acid from a lime-kiln enters through the outer concentric tube *f*. The annular space between *f* and *g* is laterally divided into two tubes *t t* (fig. 51), which pass along the main diaphragm *b* through the first three compartments, so that the weak carbonic acid enters only at the fourth compartment, but the strong carbonic acid, through *g*, at the first compartment. The inner tube bends outside the cylinder into a trough F, where the bicarbonate subsides, and where pure carbonic acid is introduced. The movement of the cylinder A is produced by means of the two hydraulic accumulators P P and the pulleys H H, so that it makes alternately half a turn to one side and then to the other. The ammoniacal brine enters through cylinder D and axle C into the last compartment of A, and passes from one compartment into another by the openings *o o*, and, finally, together with the suspended bicarbonate, into the trough F. The carbonic acid travels the opposite way, so that the liquor continually meets stronger gas, and at last pure CO_2.

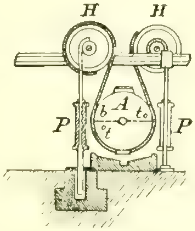

FIG. 49.

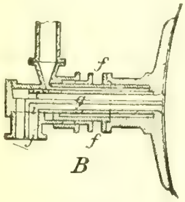

FIG. 50.

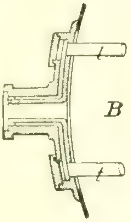

FIG. 51.

The *bicarbonate of soda*, obtained and washed on the vacuum filters or otherwise, was formerly considered quite unsuitable for sale as such, as it always smells of ammonia. Recently this drawback has been overcome, and such bicarbonate is found in trade absolutely devoid of smell (*v. Bicarbonate*, p. 480).

In order to convert the sodium bicarbonate into *commercial soda-ash* (which was formerly done with the whole of it, and is even now done with most of it), it must be dried and, by calcination, converted into normal sodium carbonate. This operation is not as easy as it would seem to be, as witnessed by the large number of patents bearing on this point successively taken out by Solvay himself and by other inventors. The salt has a tendency to form lumps, the outside of which is decomposed while the inner portion remains unchanged. This must be overcome by mechanical means. The decomposition of the bicarbonate commences at 60°C.; but in order to finish it a much higher temperature must be employed. The ammonia still contained in the salt and the carbonic acid liberated in the process must be utilised.

Fig. 52 shows one of the latest forms of apparatus for drying and calcining, described in Solvay's patent of 1879. It is a horizontal cast-iron cylinder, with an agitating-shaft *a*, heated by a fireplace *b*; the fire surrounds the cylinder and then escapes by the flue *c*. The damp bicarbonate is introduced by lateral feed-tubes *d d*, which are kept full in order to prevent any escape of gas. The calcined carbonate is pushed out by the tube *e*, reaching nearly down to the ground. Steam, ammonia, and carbon dioxide escape through *f*. The scrapers, fixed on *a*, cause the salt to travel towards the fire-end and prevent it from adhering to the cylinder. The vapours escaping through *f* are cooled down, whereupon the steam condenses with most of the ammonia in the form of bicarbonate; the carbonic acid (with traces of ammonia) is pumped away and forced into the carbonator in a place where the ammonia is already converted into normal carbonate, and where such rich gas is very efficient for effecting the conversion into bicarbonate.

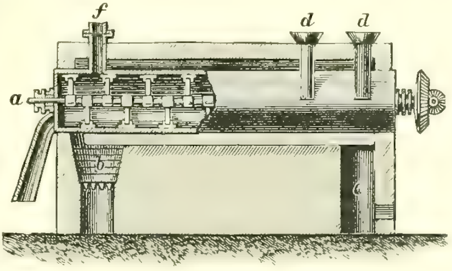

FIG. 52.

In Boulouvard's system the filtration and washing of the bicarbonate is effected by an hydraulic press, which yields drier salt than either filtration by vacuum or by the hydro-extractor (used by several other inventors). He dries and calcines the salt in very narrow cast-iron retorts (3½ inches wide and 19 inches high), six of which are joined to a common gas delivery-pipe, and are heated by a direct fire to a dark-red heat. Each retort contains about 45 lbs. of bicarbonate, and requires six hours to dry and calcine. Under these conditions the product does not form cakes.

Péchiney, in 1880, patented calcining the bicarbonate in a current of heated carbonic acid gas; this is said to yield more granular ash than the ordinary process.

L. Mond (Eng. Pat. 716, 1883) employs for calcining the bicarbonate a closed mechanical furnace, communicating with an open reverberatory furnace. In the former ammonia and carbonic acid are driven off, and in the second the calcining is finished.

Hawliczek (Eng. Pat. 9,425, 1885) proposes making soda crystals direct from the bicarbonate of the ammonia process by dissolving it in water and boiling it with constant agitation; the carbonic acid, ammonia, and steam are conveyed away, and both CO_2 and NH_3 are recovered. The residual liquor, which is generally rather greenish from tarry matters, is treated with chlorine water, and then furnishes perfectly white crystals on cooling. Mathieson and Hawliczek (Eng. Pat. 5,753, 1887) describe an apparatus for converting bicarbonate into carbonate of greater density than ordinary ammonia soda ash.

The formation of soda crystals from bicarbonate liquor has also been patented by C. D. Abel (Eng. Pat. 3,856, 1883).

The last operation is the *recovery of the ammonia from the mother-liquor*. It has been pointed out before that the success of the process depends upon keeping the loss of ammonia as low as possible. With this object the whole of the apparatus, as far as it is at all possible, is constructed in an air-tight manner, and the movement of the liquids, or even of pasty mixtures, is brought about by compressed air or gas in closed pipes and the like. Wherever any apparatus containing liquids charged with ammonia must needs communicate with the outer air, this is never done directly, but a coke-tower or other washing-apparatus, charged with a solution of salt, or with sulphuric acid, is interposed, in order to condense all the vapours of ammonia.

By far the greatest part of the ammonia is, of course, contained in the above-mentioned mother-liquor. Solvay treats this in such a way that the free ammonia, or that combined with carbonic acid, is driven out first, whereupon the 'fixed' ammonia is driven out by lime. By utilising the heat generated in slaking the quicklime and the exhaust steam of the blowing-engine, it is made possible to carry on this operation without the expenditure of fuel. The principle of Solvay's apparatus is entirely similar to Grüneberg's or Feldmann's column apparatus for working up gas-liquor, described in the article AMMONIA; but, since it had to be constructed for liquors containing a very much larger proportion of 'fixed' ammonia than is contained in gas-liquor, it presents very interesting features of its own. Solvay's apparatus will be understood from the diagram (fig. 53). The liquor passes first through a rectifying column A, where the volatile ammonia is expelled, and then successively through four cylinders, two of which, B and B^1, are shown in the diagram. These four stills, B to B^3, communicate with each other by a distributor C, similar to those used in gasworks, which permits isolating any of them without stopping the others. As a rule, one of the stills is stopped for emptying and charging while the three others are at work. The steam passes through T into C, and from this by T^1 to the longest working-still B; from here it comes out by T^2, goes again into C, and passes through T^3 into B^1; lastly through T^4 and C into B^2 (not on the diagram). From B^2 it passes through V into the column A, where it expels the volatile ammonia from the liquor running down, and imparts to that liquor a preliminary heating. In doing so the steam is condensed, and this is completed at the top by the refrigerator P, so that from A^3 only free ammonia and ammonium carbonate, but no steam, are carried into the dissolver (fig. 42, p. 497). Within P the cooling-coil S is itself filled with liquid to be distilled. The float F, in the water-vessel R, regulates the feed of liquor into A; for the more gas passes through, the warmer the water will become. The float will now descend, and it will thus work upon a cock G, which admits liquor into the coil S. The pipe L takes the liquor from S into A. Here the overflow-pipes M cause the liquor to run down while the steam and gases pass upwards through N N, and are subdivided by the perforated false bottoms X X. The liquor collects in the bottom compartment O, till there is enough for filling one of the stills, B to B^3, whereupon the valve K is closed by the lever *i*. *y* is a safety-valve at the top.

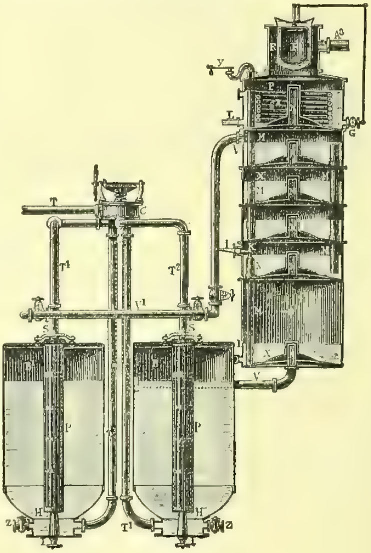

FIG. 53.

The lime required for expelling the fixed ammonia is employed in the state of quicklime, and is put through the doors S into the cages P, which retain any stones, &c. The liquor running in from O slakes the lime, and the heat thus evolved assists the distillation process. A patent of 1879 describes a method for slaking the lime by a solution of calcium or ammonium chloride, whereby a granular hydrate is obtained, which decomposes the solution of ammonium chloride more easily than the ordinary hydrate. This is effected by running the solution through a tower filled with the granular hydrate of lime, and distilling off the ammonia in another vessel.

At the end of the distillation the exhausted liquid is run off by *z*, and the bottom door I is opened so that the residual matter falls out.

L. Mond has patented a somewhat different still on the same principle as Solvay (Eng. Pat. 715, 1883).

Other inventors employ different forms of stills, all of them, however, on the 'column' principle, similar to those already described. The number of new patents in this direction is very large; Mond and Solvay themselves are constantly making fresh improvements in ammonia stills.

The liquor running away from the stills contains a large quantity of suspended matter (principally lime), and must be freed from this before being run away into any public watercourse. Solvay passes it, for this purpose, through a continuous decanter, similar to that shown in fig. 42, p. 497. The clear liquor now remaining is a solution of calcium chloride and sodium chloride, and is quite harmless. It may be deprived of the sodium chloride by boiling down and fishing out the salt, for which purpose Solvay, in 1879, described certain mechanical arrangements. The principal object of that process is to obtain calcium chloride free from sodium chloride, which in this state is better adapted for the recovery of HCl or Cl (see p. 504).

The *cost of plant* may be estimated as follows:—

Each absorbing-tower of the above-described kind (fig. 45) turns out about $2\frac{1}{2}$ tons of soda-ash in twenty-four hours. For each tower one dissolver, like RR^1 in fig. 42, and one ammonia still, like BB^1 in fig. 53, is required. The total cost of plant per ton of soda ash produced per diem is stated at 1,600*l.*, but this does not include buildings and land. The plant of the new Winnington works is constructed on a larger scale, and partly on new principles; each element produces 60 tons of soda-ash per day, and the producing-power of the works is now 10,000 tons per month.

Schloesing's process. Schloesing has introduced a modification of the ordinary ammonia process, in which first ammonium bicarbonate is formed, and is prepared in the solid state; this is then treated with a solution of sodium chloride, and thus the conversion of the latter into bicarbonate is brought about. The bicarbonate is stated to be thus obtained in a denser form than by the ordinary process. This process (patented in England in 1878, 1882, and No. 4,025, 1885) has been carried out on a large scale at Middlesbrough.

Although Schloesing's process had been previously tried on a large scale at Rouen, where a considerable sum of money had been spent upon it without attaining a commercial success, it is said to work well, but on a comparatively small scale (22 tons a week), at Middlesbrough, and it is quite possible that it would have spread much further but for the enormous capital already sunk in works built on the Solvay plan. Schloesing objects to that plan that in the beginning the ammoniacal brine absorbs CO_2 very easily, but later on with much difficulty, which entails the necessity of employing a large excess of CO_2, high towers, or similar apparatus involving pumping the gas against great pressure, and consequently expensive plant and much motive power. Schloesing avoids the necessity of employing such towers or similar apparatus by preparing ammonium bicarbonate in the following way. A solution of normal ammonium carbonate $(NH_4)_2CO_3$ is run down a coke tower, in which limekiln gases with 30 p.c. CO_2 ascend; the exit gases contain only 3 or 4 p.c. CO_2. The ammonium bicarbonate thus formed is to a great extent separated in a crystalline form. Therefore, two towers are worked in rotation. The strong gas passes first through liquor almost saturated, where crusts of bicarbonate are formed; the weak gas issuing from here acts, in the second tower, on fresh liquor, containing but normal carbonate and even a little free ammonia. On reversing the action the weak gas and fresh liquor are treated in the first tower, and the crusts of bicarbonate previously formed are thus dissolved. The warm solution coming from the strong tower is brought up to full strength in a third tower, fed with pure CO_2, produced in distilling the mother-liquors with steam and lime in columns as described above (p. 502). By fractional condensation nearly all the NH_3 is first condensed, leaving nearly all the CO_2 for the full saturation of the ammonium-carbonate liquor in the third tower, as described above. (These towers are all made of wood, about 8 feet square and 26 feet high.) The ammonium-bicarbonate solution now issues in a nearly saturated state, 40° or 45°C. warm, so that it forms, on cooling, a thick magma of crystals, which is collected on a filter and separated from the mother-liquor. When 5 or 6 tons of $(NH_4)HCO_3$ has collected on the filter, it is, without any previous washing, converted into $NaHCO_3$ by means of running a strong solution of NaCl through it. At the bottom a solution runs off, containing one-third of the NaCl unchanged (that is, as much as in the Solvay process), one-third of the ammonium bicarbonate, and all the ammonium chloride newly formed. This reaction absorbs heat, and it is necessary to supply a little external heat to obtain good $NaHCO_3$. The latter remains on the filter as a solid block of 5 tons weight, and is washed in the same spot. It is then calcined in a reverberating furnace, so that half of the CO_2 is lost with the fire gases; by employing a Thelen pan (p. 475), or similar apparatus, this loss could be avoided. Schloesing's system does away with the periodical steaming out which is necessary with the Solvay towers, and is very troublesome; it also dispenses with the large force-pumps required by the Solvay process, and is asserted to work much more cheaply in every way. The loss of NH_3 is only 0·5 to 100 Na_2CO_3. (The above is taken from notes obtained by the writer in 1889, as colleague of M. Schloesing in the Exhibition jury.)

The soda ash produced by the ammonia process is much less dense than Leblanc ash;

the latter generally has a density of about 1·2, the former only of 0·7 to 0·8. This causes, in the first instance, a greater expense for packages. Moreover, those consumers who require soda ash for igneous processes, as glass and ultramarine makers, complain that the ammonia ash is more easily carried away by the draught; that the crucibles or retorts take a much smaller charge, and are less easily heated, through the mass being too porous. Even the absence of the small quantity of caustic contained in Leblanc ash, which for some of its uses is objectionable, is a drawback militating against ammonia ash in the above-mentioned cases, because caustic renders the ash more fusible.

These objections have been to a great extent overcome by a subsequent furnacing of the ammonia ash, which renders it denser, by mechanically compressing it in the casks, and, where necessary, by directly mixing it with the requisite quantity of caustic soda.

In most respects ammonia ash is preferred to Leblanc ash, owing to its great strength and purity. It is now regularly guaranteed at 98 to 99 p.c.; such ash, according to an analysis by Pattinson, contained, for instance:—

Sodium carbonate	98·72
„ chloride	0·54
„ sulphate	0·20
Magnesium carbonate	0·04
Calcium carbonate	0·13
Ferric oxide	0·01
Alumina	0·01
Silica	0·09
Moisture	0·32

The entire absence of caustic (instead of which there is generally a very slight percentage of bicarbonate present) is a special recommendation for bleachers and for various chemical purposes.

The quantity of salt decomposed in the ammonia-soda industry in the United Kingdom amounted to:—

In 1884	80,759 tons
„ 1885	115,032 „
„ 1886	137,220 „
„ 1887	158,636 „
„ 1888	212,181 „

The total production of the works connected with the Solvay Company (not counting that produced by other processes) has been stated by that Company as amounting in 1889 to the following figures:—

Belgium	17,000 tons
France	100,000 „
England	125,000 „
Germany	100,000 „
Russia	17,000 „
United States	60,000 „
Austria	11,000 „
	430,000 tons.

The quantity of ammonia soda made by other processes in Germany amounts to about 50,000 tons; in France rather less. In fact, the total quantity of salt consumed for ammonia soda in France in 1887 was 152,202 tons, in 1888 155,902 tons, which would not yield more than 80,000 tons, or less than the Solvay works are claimed to have made by themselves in 1890.

The recovery of hydrochloric acid, or chlorine, in the ammonia-soda process.

1. *From the calcium chloride of the ordinary ammonia-soda process.* The solution of this problem (which is also referred to in the article Chlorine) has been attempted in various ways. Solvay has taken out several patents—in 1877 and later—for liberating hydrochloric acid from $CaCl_2$ by ignition with sand, clay, &c., in a current of superheated steam:

$$CaCl_2 + SiO_2 + H_2O = CaSiO_3 + 2HCl.$$

The hydrochloric acid obtained in this way is very much diluted with hot steam &c., and its recovery is therefore incomplete and expensive.

Solvay has latterly introduced the simultaneous action of heat and air upon the calcium chloride, and has actually obtained chlorine in this way on a large scale; but it is doubtful whether this is an economical process; it is certainly not yet introduced anywhere in current work.

Tacquet (Germ. Pat. 30,832) heats the dry calcium chloride obtained from the waste liquor of the ammonia process with silica and manganese dioxide to obtain chlorine:

$$CaCl_2 + MnO_2 + 2SiO_2 = Cl_2 + CaSiO_3 + MnSiO_3.$$

This process, in which the manganese is lost, is evidently hopeless.

2. *By employment of magnesia.* Weldon, in 1872, about the same time as Solvay, patented the use of magnesia in lieu of lime for decomposing the ammonium-chloride liquor, with a view of recovering from $MgCl_2$, by well-known means, both MgO and HCl. This is nothing like so easy as was formerly imagined, and all endeavours in that direction have failed. But these labours of Weldon, pursued and enlarged by Péchiney, have ultimately led to the working-out of a process for decomposing magnesium oxychloride by heat and air for the direct preparation of chlorine, as described in the article Chlorine.

That process, so far, has been carried out only with magnesium chloride from the mother-liquors of the manufacture of sea salt, or of potassium chloride from the Stassfurt carnallite. Before it could be applied to the ammonia-soda process it would have to be seen whether the magnesia recovered by the Péchiney process is sufficiently active for decomposing the ammonium-chloride liquor.

Another process, by Schloesing, begins with drying the magnesium chloride in an atmosphere of HCl; thus anhydrous $MgCl_2$ can be obtained, which, on heating in a current of air, readily yields up its chlorine. There are evidently great technical difficulties to be overcome in the first part of the process.

3. *By decomposing the ammonium chloride with sulphuric acid.* L. Mond, in 1883, patented the following process: The mother-liquor of the ammonia-soda process is first distilled till all ammonium carbonate has been expelled (and recovered), and is further concentrated, always fishing out the sodium chloride formed, till dry ammonium chloride has been obtained. This is heated with enough sulphuric acid to expel all

hydrochloric acid and form acid ammonium sulphate $(NH_4)HSO_4$, which is either converted by free ammonia into ordinary commercial sulphate or is used for dissolving phosphates. This process is evidently incapable of being applied to any large works, since it involves the manufacture of enormous quantities of ammonium sulphate or superphosphate.

4. *By phosphoric acid.* O. N. Witt (Germ. Pat. 34,395) proposes decomposing the ammonium chloride by phosphoric acid, which drives off the HCl; after this the residual ammonium phosphate is brought to a higher temperature, and now gives up its ammonia; the vitreous phosphoric acid remaining behind serves as before. This process has been investigated by Jurisch (D. P. J. 267, 424). According to him, 99 p.c. of the HCl can be driven off at about 300°C. if a very large excess of phosphoric acid is employed; the residue consists of 4 mols. free phosphoric acid, 4 mols. ammonium phosphate, and 2 mols. ammonium pyrophosphate. By heating this further to about 400°C., 63·6 p.c. of the ammonia is driven off. When employing the residue over again, 86 p.c. of the total ammonia can be driven off. Silver or platinum vessels are strongly acted upon, and there is no other material known which resists the action of fusing phosphoric acid, so that there seems to be no way of carrying out Witt's process in actual practice.

A number of inventions in this line depend upon the fact that in volatilising ammonium chloride it is split up into NH_3 and HCl, which by suitable means can be separated. There was, however, no material known which could furnish vessels to resist the action of NH_4Cl in volatilising. Mond (Eng. Pat. 2,160, 1889) has shown that antimony can serve this purpose.

Combinations of the ammonia process with the Leblanc process.

(1.) *Applying the ammonia process to sulphate of soda.* Sulphate of soda, in a solution saturated at 34°C., is easily converted into bicarbonate by ammonia and carbonic acid. This fact has been utilised in the process of C. H. Gaskell and F. Hurter (No. 5,712, 1883; No. 8,804, 1884; No. 9,208, 1886). They found that ammonium sulphate and sodium sulphate, when heated together in a current of steam, are completely decomposed into free ammonia and sodium bisulphate. The latter is heated with common salt, when hydrochloric acid is set free and sodium sulphate is recovered. The reactions of the process are, therefore:

1. $Na_2SO_4 + 2NH_3 + 2CO_2 + 2H_2O = 2NaHCO_3 + (NH_4)_2SO_4$.

2. $(NH_4)_2SO_4 + Na_2SO_4 = 2NH_3 + 2NaHSO_4$.

3. $NaHSO_4 + NaCl = HCl + Na_2SO_4$.

This very ingenious process does not seem to work smoothly and cheaply enough to compete with the Dyar and Hemming process. The second reaction (an endothermic one) seems to cost too much time, coal, and steam. For the conversion of sodium sulphate into carbonate the following prescriptions are given: A hot solution of sodium sulphate, 50–60°Tw. strong, is purified from iron, lime, and free acid by adding a sufficient quantity of soda, and is cooled down to 38°C. It is then treated with ammonia till 24 or 25 parts of NH_3 are present to each 100 of Na_2SO_4. The temperature should be between 32° and 38°C. At the same time carbonic acid is introduced, and when ammonium monocarbonate has been formed the further introduction of CO_2 must take place under pressure. As soon as sodium bicarbonate begins to separate the liquid is allowed to cool down.

(2.) *Employment of Leblanc alkali waste in the ammonia process.* Schaffner and Helbig (Germ. Pat. 19,216) proposed decomposing alkali waste with magnesium chloride, as in their sulphur-recovery process (*cf.* p. 491). The magnesia formed, together with another quantity produced from the magnesium chloride in excess by addition of lime or dolomite, is used for decomposing the ammonium-chloride liquor, and thus magnesium chloride is regenerated.

Parnell and Simpson (Eng. Pat. 381, 1,937, 7,657, 8,440, all of 1885; 46 and 47, of 1886; 2,831, 4,648, 6,175, of 1888) decompose the ammonium-chloride solution directly with Leblanc tank waste. Their process has undergone several variations; that which they seem to have ultimately adopted is as follows: Ammonium-chloride liquor is treated by tank waste, whereby ammonium sulphide is given off: $2NH_4Cl + CaS = CaCl_2 + (NH_4)_2S$. The vapour is absorbed in water or in a weak ammoniacal solution until it contains from 8 to 10 p.c. of ammonia. This strong solution is cooled down and subjected to a current of pure carbonic acid (prepared as below), until crystals of ammonium bicarbonate are formed and hydrogen sulphide is given off: $(NH_4)_2S + 2CO_2 + 2H_2O = 2(NH_4)HCO_3 + H_2S$. The latter, after being washed to arrest any carbonic acid and ammonia, is conducted into a gas-holder for use. The ammonium bicarbonate crystals, together with a portion of the mother-liquor, are removed from the carbonating apparatus, and after draining are agitated in a solution of sodium chloride, when sodium bicarbonate is formed, which is afterwards converted into monocarbonate. The ammonium chloride remaining in the mother-liquor enters again into the cycle of operations by being heated with tank waste, and so forth. The ammonia which is removed in the form of bicarbonate and mother-liquor from the carbonating apparatus is compensated for by the addition of ammonium sulphide, so that the strength of the ammoniacal liquor is maintained at the same degree. The mother-liquor from the carbonating apparatus is used for absorbing the ammonium sulphide given off in the first stage of the process.

In order to obtain pure carbonic acid, lime-kiln gases, or the like, after washing and cooling, are brought into contact with a cold aqueous solution containing 25-30 p.c. ammonium carbonate, taking care that the temperature never exceeds 21°C. Crystals of ammonium bicarbonate are formed, which are separated from the mother-liquor and heated to 74°C. in a closed vessel. Carbonic acid, with a little ammonia and steam, is evolved. The gas is cooled, returning the condensation products to the heating vessel, is washed with acid, water, or brine, to deprive it of ammonia, and is then ready for use. The liquor remaining in the heating vessel is cooled, when it deposits a second crop of ammonium bicarbonate crystals, and the mother-liquor returns to the absorbing apparatus for carbonic acid. (Those processes have not extended beyond the works where they have originated.)

Statistics of the manufacture of alkali.

The returns of the Alkali Manufacturers' Association show the amount of the various products of the soda industry annually produced from the year 1877 to 1886 in the United Kingdom:—

Year	Salt decomposed	Alkali, 48 p.c. Leblanc process	Alkali, 48 p.c. Ammonia process	Soda crystals	Caustic soda, 60 p.c.	Bleaching powder[1]	Bicarbonate of soda
	tons	tons	tons	tons	tons	tons	tons
1877	578,201	217,556	6,220	169,769	74,663	105,529	12,109
1878	568,542	196,876	11,116	170,872	84,612	105,004	11,756
1879	615,287	230,683	15,526	185,319	86,511	115,290	13,083
1880	700,016	266,093	18,800	192,926	106,384	131,606	13,539
1881	675,099	238,687	20,400	203,773	108,310	135,826	12,853
1882	679,935	233,213	39,000	180,846	116,864	135,170	14,115
1883	705,732	227,284	52,750	188,678	119,929	141,868	13,609
1884	690,502	204,072	61,480	182,567	141,639	128,651	14,576
1885	722,472	184,597	77,530	202,705	144,954	132,761	15,179
1886	713,112	165,782	85,000	182,379	153,884	136,234	15,083
1887	731,199	255,272		?	169,463	139,925	?

[1] This includes chlorate of potash, taking 5 tons of bleaching powder for 1 ton of chlorate. The amount of chlorate now made is equal to 7,000 tons per annum.

The development of the German alkali trade is best illustrated by the official returns. In 1876 (the last year for which full statistics are given in Lunge's Alkali, 3, 73) the excess of importation into Germany over the quantity exported from the same country was as follows:

Soda ash	15,171	tons
Caustic	8,073	,,
Crystals	14,327	,,
Bicarbonate	529	,,

But the official statistics for 1891 are as follows:—

—	Excess of exportation over importation	Excess of importation over exportation
	tons	tons
Soda ash	35,131	—
Soda crystals and crude soda	7,785	—
Caustic	2,763	—
Bicarbonate		37
Saltcake (including nitre-cake)	26,960	—
Hydrochloric acid	5,500	—
Sulphuric acid	9,436	—
Bleaching powder	—	2,075

Hasenclever (Chem. Indust. 1887, 290) estimates the German production of soda ash, caustic, crystals, and bicarbonate, all reduced to 100 p.c. Na_2CO_3, at 150,000 tons (=187,500 tons 48 p.c. soda ash), against only 42,500 tons in 1878. About 75 p.c. of the German production is ammonia ash (against 60 p.c. in France, 47 p.c. in Austria, 22 p.c. in Great Britain). There are in Germany 9 works making only ammonia ash, 7 only Leblanc ash, and 3 both. While in 1878 the importation into Germany exceeded the export to the extent of 27,000 tons (calculated at 100 p.c. Na_2CO_3), she exported in 1886 10,204 tons over and above the imported quantity.

The price per 100 kilos. of soda ash has in the same period gone down from 20 marks to 8 marks. The value of hydrochloric acid, on the other hand, has risen to such an extent that several industries depending upon its use, such as the recovery of sulphur by Mond's process, have had to be given up to a great extent. Sulphurous and sulphuric acids now replace hydrochloric acid in many cases.

The *cost* of raw materials for producing a ton of 48 p.c. soda ash in Lancashire in 1861 and 1886 is stated by E. K. Muspratt (S. C. I. 1886, 411) as follows:—

1861.

	£	s.	d.
$1\frac{1}{4}$ ton pyrites (Irish)	1	15	0
1 cwt. nitrate of soda	0	12	0
$1\frac{1}{4}$ ton salt	0	10	0
$1\frac{1}{2}$ ton limestone	0	10	0
$3\frac{1}{2}$ tons fuel	1	1	0
	£4	8	0

1886.

	£	s.	d.
$13\frac{1}{4}$ cwt. Spanish pyrites (sulphur value)	0	9	3
23 lb. nitrate of soda at 10*s*.	0	2	0
25 cwt. salt at 8*s*.	0	10	0
26 cwt. limestone at 5*s*.	0	6	6
$2\frac{3}{4}$ tons fuel at 4*s*. 6*d*.	0	12	6
	£2	0	3

This shows that, although the price of the raw materials had not materially decreased during the intervening twenty-five years, excepting that of pyrites (as detailed in the original), the improvements in manufacturing processes had led to the cost of those materials for a given production being lessened by more than half. On the other hand, the prices of manufactured articles have changed as follows:

—	1827–1830	1839–1840	1878	1886
Soda ash	£16 10*s.*	£15	£5 10*s.* to £6	£4 to £4 10*s.*
Soda crystals	£18 10*s.*	£11	£3 12*s.* 6*d.*	£2 15*s.*
Caustic soda, 70 p.c.	—	—	£12 10*s.*	£8 5*s.*
Bleaching powder	—	£19	£5	£5 17*s.* 6*d.*
Brown vitriol, ¾*d.* to 1*d.* per lb. . .	—	—	£3	£2
Saltcake	£7 10*s.*	£6 10*s.*	£2	£1 5*s.*

Hasenclever (Chem. Ind. 1880, 239) gives the following comparison of the cost (in Germany) of Leblanc soda and ammonia soda per 100 kilos. of pure sodium carbonate (100 p.c. = 58·5 English degrees):—

—	Price per ton, in marks (= 11¾*d.*)	—	Leblanc soda	—	Ammonia soda
		kilos.	value (marks)	kilos.	value (marks)
Coals . . .	8	400	3·20	210	1·68
Limestone . .	2	175	0·35	166	0·33
Salt . . .	15	150	2·25	220	3·30
Pyrites . . .	20	110	2·20	—	—
Nitre . . .	300	1·5	0·45	—	—
Ammonium chloride	300	—	—	5	1·50
Wages . . .	—	—	2·00	—	1·00
	—	—	10·45	—	7·81

Deduct hydrochloric acid, 250 kilos. at 1 M. = 2·50
Deduct recovered sulphur, 15 kilos. at 3 M. = 0·45 2·95

7·50 Marks.

G. L.

Sodium biborate, or **Borax.** Borax occurs in the crude state on what are termed borax marshes, which are generally the bottoms of dried-up lakes, or, where tincal is found, lakes that are nearly dried. The crude borax in the former instances is found lying on the surface of the plain, of a peculiar greyish-yellow colour, having a depth of from one inch to eighteen inches. It is generally associated with other impurities, both soluble and insoluble, as the following table of analyses shows:—

Composition of crude borax from the marshes.

—	1	2	3	4	5	6	7	8
Sodium biborate	30·30	38·3	2·10	53·08	1·9	33·30	6·52	45·20
Water	37·68	40·8	14·08	39·24	25·7	25·88	16·46	43·80
Sand and insoluble matter . .	18·00	10·9	12·80	1·20	33·0	2·40	8·80	7·15
Sodium carbonate	6·10	5·3	16·10	5·50	34·3	13·70	18·30	2·75
Sodium sulphate	·26	·1	19·10	·35	·5	8·25	20·22	
Sodium chloride	·50	·4	34·60	·50	·7	15·40	28·20	·40
Calcium carbonate	3·28	2·4	·70	—	2·0	·60	·80	·30
Magnesium carbonate . . .	2·26	·4	·30	—	·6	·30	·50	·30
Oxide of iron and alumina . .	1·62	1·4	·22	·13	1·3	·17	·20	·10
	100·00	100·0	100·00	100·00	100·0	100·00	100·00	100·00

At Jagadhri, in Northern India, 37 miles S.E. of Umballa, there is a borax refinery, the product of which is shipped to Calcutta. The quantity of tincal and borax obtained from the districts of the Himalayan mountains amounts to about 2,000 tons per annum. The tincal deposits are of very ancient origin. In North America there are no less than ten deposits, five of them being in the State of California—at Saline Valley, Furnace Creek, and Armagora (in Inyo county), Slate Range (in San Bernardino county), and Lower Lake (in Lake county); the remaining five are in the State of Nevada—at Rhodes, Teels Marsh, Columbus, and Fish Lake (in Esmeralda county), and Salt Wells (Carson Lake, Churchill county).

Borax was first accidentally discovered in California, in 1856, by Dr. John A. Veatch, since which time the different deposits mentioned have been developed, the quantity produced amounting to about 4,000 tons annually, although the available supply is practically unlimited, and is solely regulated by the demand. The sp.gr. of borax is 1·73. The anhydrous salt $Na_2B_4O_7$ has a sp.gr. of 2·367, the composition being:

Boracic acid B_2O_3	69·05
Soda Na_2O	30·95
	100·00

Table of the solubility of borax in water.

Temperature Centigrade	100 parts of water dissolves $Na_2B_4O_7$	100 parts of water dissolves $Na_2B_4O_7 10H_2O$
0°	1·49 parts	2·83 parts
10°	2·42 ,,	4·65 ,,
20°	4·05 ,,	7·88 ,,
30°[1]	6·00 ,,	11·90[1] ,,
40°	8·79 ,,	17·90 ,,
50°	12·93 ,,	27·41 ,,
60°	18·09 ,,	40·43 ,,
70°[1]	24·22 ,,	57·85[1] ,,
80°	31·17 ,,	76·19 ,,
90°	40·14 ,,	116·66 ,,
100°	55·16 ,,	201·40 ,,

We will first indicate the principal sources and characters of the raw materials employed in the manufacture of borax before describing the process of making that salt.

Boracic acid $B_2O_33H_2O$. The most abundant source of supply at present is that of Central Italy, where it is produced on a large scale in the territories of four communes: Pomerance, Massa Marittima, Castel Nuovo di Val di Cecina, Montieri, all in the province of Tuscany, the nearest shipping point being Leghorn, to which place it is brought by railroad from Volterra, the amount annually produced averaging 3,000 tons. It also occurs in the extinct crater of a volcano on one of the Lipari Islands, and in the crater of Stromboli, an active volcano on another island of the same group, near Sicily. It exists in solution in the mineral waters of Wiesbaden, Aachen, and Krankenlied, in Germany; in the mud volcanoes of the Colorado desert, in San Diego county, California; in the water of several mineral springs in Tehama county, California; in the waters of the Mediterranean Sea and Pacific Ocean.

Sassolin, or Tuscan boracic acid, is never produced in the pure state, but is always associated with impurities, both soluble and insoluble. It differs considerably in quality, some parcels containing 89 p.c. of crystallised acid, while others yield only 75 p.c. The following analyses show its general composition:—

Analyses of crude Tuscan boracic acid.

Boracic acid B_2O_3	47·95	44·04
Water, hygroscopic	37·00	33·98
Water, combined	·73	2·80
Ammonium sulphate $(NH_4)_2SO_4$	5·67	10·62
Sulphate of alumina and iron	·13	·20
Calcium sulphate	trace	1·20
Magnesium sulphate	6·91	4·03
Sodium sulphate	·07	1·10
Sodium chloride	·23	·32
Sand	·42	·80
Sulphur	—	trace
Organic matter	·89	·91
	100·00	100·00

An analysis of an average sample taken from 5,000 tons shows it to be composed as follows:

Crystallised boracic acid $B_2O_3.3H_2O$	83·46
Hygroscopic water	1·40
Ammonium sulphate	5·30
Magnesium sulphate	7·50
Iron and alumina	·30
Sand, organic matter, &c.	2·00
	100·00

Table of the solubility of boracic acid in water.

Temperature Centigrade	Solution in parts of water	100 parts of water dissolve	Saturated aqueous solution contains p.c. $B_2O_33H_2O$
18·7°	25·66	3·9 parts	3·73
25·0°	14·88	6·8 ,,	6·27
37·0°	12·66	7·8 ,,	7·32
50·0°	10·16	9·8 ,,	8·96
62·5°	6·12	16·0 ,,	14·04
75·0°	4·73	21·0 ,,	17·44
87·5°	3·55	28·0 ,,	21·95
100·0°	2·97	34·0 ,,	25·17

Boracic acid evaporates freely in a current of steam. The loss sustained by evaporating an aqueous solution is ·28 p.c. of the water evaporated, equal to 2·8 lbs. for every 100 gallons.

Calcium borates $Ca_2B_6O_{11}$. There are three varieties of calcium borate, which correspond to the three varieties of calcium carbonate, calc spar, marble, and chalk—viz. *boracite, colemanite*, and *pricite*—each found in different parts of the world in large quantities, and of a well-defined and constant composition. *Boracite*, in outward appearance, closely resembles a snow-white, fine-grained marble; *colemanite* is of a crystalline nature like calc spar, or Iceland spar, and has been termed *borate spar*; *pricite*, or *bechilite* is a very fine, white, soft, chalky mineral of a cohesive nature, easily rubbed to powder, and resembling chalk. Chemically speaking, they are all hydrated sesquiborates of lime, differing only in their composition in respect to the water of combination, their composition being given in table on following page.

Boracite has been extensively mined for several years (since 1869) at Sultan-Chairi, in the district of the Villayet of Brousa, in Asia Minor, forty-five miles from Panderma, a port on the Sea of Marmora; the principal deposits, as far as yet known, exist near the Tschataldga Mountain in longitude 28° 2″ east of Greenwich and latitude 40° north. The Susurlu river runs from the Tschataldga Mountain to the Sea of Marmora; it is partly navigated to a point called Mohalitch; the field is situated in a basin of tertiary age, surrounded by volcanic rocks, which vary from granite on the east to trachyte on the north, and columnar basalt on the west. Several basaltic hills and dykes protrude in different portions of the basin, and the presence of hot and mineral springs further testifies to the volcanic influences which have been at work, and in which doubtless originated the boracic mineral. The latter occurs in a stratum at the bottom of an enormous bed of gypsum; its greater sp.gr. probably impelling it down-

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[1] At the temperature of 27°, borax solutions hold 1 lb. of borax to the imperial gallon, and have a sp.gr. of 1·050 or 10°Tw. The general crystallising strength is 1·160 sp.gr., or 32°Tw., when the solution holds 5 lbs. of borax to the gallon, crystallisation commencing at 65·5°.

	$Ca_2B_6O_{11}3aq$	$Ca_2B_6O_{11}4aq$	$Ca_2B_6O_{11}5aq$	$Ca_2B_6O_{11}6aq$
Boracic acid B_2O_3	55·8	53·3	50·9	48·8
Lime CaO	30·0	28·4	27·2	26·1
Water H_2O	14·2	18·3	21·9	25·1
	100·0	100·0	100·0	100·0

wards, while the whole mass was yet in a soft state. Several feet of clay cover the gypsum bed, which is here 60 or 70 feet thick, though in places it attains to double that thickness. The borate strata vary in depth, and have been proved for a vertical distance of 45 feet. The mineral exists in closely packed nodules of very irregular size and shape, and of all weights up to a ton. It is easily separated from the dark-coloured gypsum in which it is embedded, and a number of people are employed at the pit mouth in picking and selecting the material. About eight thousand tons are extracted from these mines yearly, the material being carted to Panderma for shipment; it is sold on a basis of 40 p.c. boracic acid, which would be equal to 78·5 p.c. of the pure calcic sesquiborate with five molecules of water $Ca_2B_6O_{11}5aq$, the remainder consisting of calcium sulphate and other impurities.

Borate spar or *colemanite* has been extensively mined since 1883 at Calico, in San Bernardino county, California, 462 miles south-east of San Francisco. The geological formation of the surrounding hills consists of black lava, sandstones of different colours, gypsum, steatite, and calcium carbonate; it is found in veins and seams from 2 feet to 8 feet in thickness, in some cases dipping at an angle of 36°, and at others running into the hillsides almost horizontally. Its colour and streak is white-milky to transparent; hardness 3·5–4; sp.gr. 2·4; before the blowpipe exfoliates, decrepitates violently and melts imperfectly after considerable heating; it imparts a reddish-yellow colour to the flame, which changes to green. The mineral pulverises easily, fragments obscurely rhombic, it is wholly soluble in hot hydrochloric acid; from the solution boracic acid crystallises on cooling. Lustre of the mineral is vitreous to adamantine, exhibiting many specimens of perfect crystals. The veins and seams are interspersed with masses of calcium carbonate and magnesium silicate, from which, like the boracite, it has to be picked and selected. As much as 2,500 tons per annum have been taken from these mines.

Its formula is $Ca_2B_6O_{11}5aq$; it is sold on the basis of 40 p.c. boracic acid. Average samples from the bulk vary in composition from 33·8 p.c. of boracic acid up to 41·2 p.c.; the following analyses may serve as examples of the general composition:—

Borate spar.

Component parts	1	2	3	4	5
* Calcium sesquiborate $Ca_2B_6O_{11}5aq$.	66·2	70·4	75·0	78·00	80·80
Calcium carbonate $CaCO_3$ . .	16·3	15·1	11·6	8·75	7·17
Insoluble matter SiO_2	10·5	10·2	8·9	7·10	7·60
Remaining impurities MgO, &c. .	7·0	4·3	4·5	6·15	4·43
—	100·0	100·0	100·0	100·00	100·00
* = to boracic acid	33·8 p.c.	35·9 p.c.	38·2 p.c.	39·8 p.c.	41·2 p.c.

Borate spar is also found in the neighbourhood of Furnace Creek, Inyo county, California; its outward appearance is frequently so exactly like calc spar as often to be mistaken for that mineral. Pricite has hitherto not been so extensively mined as boracite and colemanite; a mine of this mineral, however, is being worked at Lone Ranch, Cheteo, Curry, county Oregon, from which source, since the first cargo was extracted by E. L. Fleming in 1888, several hundred tons have been taken out. It is found embedded in boulders of different size, the nodules varying in weight up to one ton. It is of a soft chalky nature, purely white, can be easily rubbed to powder, but is of a cohesive character; it is very soluble in sulphurous acid, hydrochloric acid, or acetic acid, yielding boracic acid. The following analysis from bulk shows its composition:—

Boracic acid B_2O_3	44·24
Lime CaO	30·91
Water H_2O	23·00
Magnesia MgO	·65
Silica SiO_2	1·20
	100·00

Bechilite is a calcium borate found in the lagoons in Tuscany.

Mr. N. H. Darton (Am. S. 1882) describes a mineral from Bergen Hill, New Jersey, United States.

The composition of both these minerals may be represented by the formula CaB_4O_75aq:

Boracic acid B_2O_3	48·9
Lime CaO	19·6
Water H_2O	31·5
	100·0

Boronatrocalcite. Ulexite, tiza, cottonballs, $Ca_2B_6O_{11}Na_2B_4O_7 16aq$ (*hayesin*) is a soft, fibrous, silky mineral of a brilliant white when pure, generally found in nodules of a yellowish white colour, varying in size from that of a Brazil nut to a potato. This curious mineral was first found in the nitre beds of Peru in small quantities, and was examined by Ulex in 1836. It was discovered in Tarapaca, 30 miles from Iquique, under the crust that covers the nitrate of soda beds. It has since been discovered in Chili, Bolivia, California, Nevada, Nova Scotia, and Persia.

Its composition is constant, containing, when pure—

Boracic acid B_2O_3	43·1
Lime CaO	13·8
Soda Na_2O	7·7
Water H_2O	35·4
	100·0

The nodules frequently are found incrusted with a coating of sodium sulphate and salt, from which cause the percentage of boracic acid in large parcels varies considerably, the average being from 18 to 25 p.c.

Chili has hitherto been the principal source of supply of this borax material, from 2,000 to 3,000 tons being extracted annually and shipped from the ports of Iquique and Caldera. Ulexite, when in a state of fine division, is difficultly soluble in boiling water.

Magnesium borate. Stassfurtite (*Szaibelyte*). This mineral occurs crystalline and massive, colour white, streak white, fracture conchoidal uneven, subtransparent, translucent, lustre vitreous inclining to adamantine, hardness 7, sp. gr. 2·83, pyro-electric, soluble in acids. It is found at Stassfurt, Prussia, embedded in the kainite beds, the composition being—

Boracic acid	62·33
Magnesia	27·03
Chlorine	7·91
Magnesium	2·73
	100·00

It is also found in nodules in gray limestone at Werksthal, Hungary, and at Danbury, Connecticut, United States.

Calcium borosilicate. Dotolite (*Howlite*). A siliceous borate of lime, colour white, streak white, opaque, of a chalky nature, found at Calico, San Bernardino County, California, and at Brookville, Nova Scotia. Composition—

Boracic acid	44·22
Lime	28·69
Silica	15·25
Water	11·84
	100·00

Ammonium borate. Larderellite. A mineral found in the lagoons of Tuscany. It occurs in small crystalline rhomboidal plates.

Boracic acid	68·556
Ammonia	12·734
Water	18·325
	99·615

Lagonite is a borate of iron, also found in the Tuscan lagoons. *Sussexite* is a newly discovered hydrated borate of manganese and magnesia found in Sussex County, New Jersey, United States. Tourmaline, found in different parts of the world in different colours, also contains a small percentage of boracic acid.

The manufacture of borax from boracic acid.

This industry is chiefly associated with the production from the Tuscan lagoons. The crude acid, packed in large casks weighing about 13 cwt., on arrival at the borax works is first of all manipulated in the casks themselves. For this purpose, the cask is placed on what is termed a stillage, the head taken off, the acid loosened with a spade and treated with small quantities of water for the purpose of washing out the sulphates of ammonia and magnesia, which, on account of their superior solubility easily separate from the less soluble boracic acid, the washings being used for the recovery of the ammonia and magnesia they contain, whilst the acid, which formerly contained 83·46 p.c. $B_2O_3 3aq$, or equivalent to 128·5 p.c. borax, is brought up to a strength of 96·67 p.c. $B_2O_3 3aq$, or equivalent to 148·87 p.c. borax. The acid, after draining for twenty-four hours, is then placed in wicker baskets and transferred to the saturators. These are made of wrought-iron $\frac{3}{8}$ plates, having a diameter of ten feet, egg-ended, height 9 feet 6 inches, provided with hopper and swivel discharge, still head, inspection glasses, run off stop-cocks, and connected by steam pipes with a perforated iron coil in the bottom of the pan for the purpose of boiling the borax liquor with injected steam. There is also a manhole with movable cover. When the saturator is ready for charging, liquor is pumped in to the height of four feet, or 2,300 gallons, which is then boiled with steam and soda ash. The anhydrous carbonate of soda is added, about 23 cwts. being generally required to 60 cwts. of acid. When the soda ash is all dissolved the manhole lid is placed on, and the boracic acid is put in by degrees through a hopper, half a hundredweight at a time. At each addition of acid a brisk ebullition of carbonic acid takes place, which passes along the still head, and after being deprived of its ammonia is utilised for making bicarbonate of soda.

After the saturator has received its charge of soda ash and acid the liquor is thoroughly boiled for five hours and allowed to settle, in order that the solid impurities may subside. This generally occupies from eight to ten hours, after which the liquor is run into large wrought-iron vats twelve feet long, six feet wide, four feet deep, into which the wires made of iron, technically called 'straps,' are suspended over bars of wood laid across the top of the vat. The liquor on cooling crystallises on the wires, sides, and bottom of the vat, and when the temperature has fallen to 26° (80°F.) the liquor is siphoned off from the vats, and men get in, and, by the aid of iron bars terminating in a chiselled end, first remove the crystallised borax from the straps, then cut up the borax crystallising on the bottom of the vat, and lastly knock down the sides. This borax is not of sufficient purity for the market, and is, therefore, subjected to a second refining, and, if necessary, bleaching. For this purpose a series of pans, called refining pans, are employed; they are also of wrought-iron, circular, 9 feet diameter, egg-ended, 8 feet deep, open at the top and provided with cradles of wrought iron, perforated with holes suspended by iron chains from a patent block overhead in such a manner as to be raised or lowered in the pans as required. The pans are boiled with steam issuing from a perforated pipe in the bottom. They are first half filled with water, or some of the clearest liquor from a previous operation, and when the liquor is boiling crude borax is thrown into the crádle and allowed to dissolve. The right amount of borax is tested by means of the Twad. hydrometer, which should mark when the liquor is of the required strength, 30°. About 5 cwts. of carbonate of soda is added, and a little chloride of lime, and the whole thoroughly boiled. The saturated liquor is then allowed to settle in the pans for ten hours, covers being placed on them to prevent the liquor chilling; the pans are run off into vats of similar size and shape to those employed in the first process, and the borax allowed to crystallise, which takes six days. Upon the expiration of that time, the liquor is siphoned off to a well, made by sinking a wrought-iron tank in the ground below the level of the vats, and if impure is pumped up to the refining pans to be used over again, and if sufficiently pure is pumped to boiling-down pans, to be concentrated to such a degree as to yield a further crop of borax.

The liquors from the first vats are also pumped to the boiling-down pans, where they likewise undergo a process of concentration. These boiling-down pans are made of wrought iron, and are capable of holding about 4,000 gallons. They are provided with dry steam coils, and are superior to other means of concentration from the fact that they are completely under control, and the evaporation of the liquor can be regulated as fast or as slow as may be necessary. The liquors in these pans are concentrated until they reach a sp.gr. of 1,300, or 60° Tw., when they are run off into vats to yield first a crop of borax, and then upon reaching a temperature of 80° Fah. they are siphoned off into other vats where they yield a crop of Glauber salts, or sodium sulphate, after which the liquors, being rich in sodium carbonate, are used again in the saturators for making up a fresh batch of borax with acid and soda ash. The mother-liquors strong in common salt and weak in sodium carbonate are further concentrated in jacketed pans, where, on continued boiling, the salt falls to the bottom, is collected by means of rakes, and fished out with perforated scoops provided with long wooden handles, and the salt is ladled into iron baskets set over the pans and allowed to drain. By this means all the salts contained in the soda ash and boracic acid are saved, and nothing is run to waste.

The washings from the boracic acid in the first process, containing the sulphate of ammonia and sulphate of magnesia, are collected together, and placed in a wrought-iron still provided with a dry steam coil. The requisite amount of sodium carbonate is then added, and the ammonium carbonate is distilled off, yielding a highly concentrated and very pure carbonate of ammonia liquor, which is either sold in that state or utilised for making the purest volcanic ammonia salts.

The borax from the refined vats, consisting of the straps and sides, is carried to the packing room, there to be picked, selected, and packed in casks, whilst the borax bottoms, not being in the form of merchantable borax, are refined again.

Manufacture of borax from sesquiborate of lime.

The mineral is first crushed in a stone breaker, the size of jaws being eight inches and known as a number 4, easily capable of crushing twelve tons in twenty-four hours. As the mineral passes through it is taken up by an elevator and run through millstones, thirty inches in diameter, and placed by the side of the crusher. There are two pairs, one grinding fresh ore and the other grinding the tailings. The millstones deliver the powdered ore into another elevator, which passes it through a bolting or sifting machine, ten feet long, thirty inches diameter, having octagonal sides, the bolting cloth being of silk known as No. 8. As considerable fine and impalpable dust arises from the sifting, it is kept down by means of an exhaust fan blowing the dust into a dust room. The fine mineral is conveyed by means of an Archimedean screw and elevator into bins, each holding a certain quantity and placed over the saturators. These are wrought-iron tanks capable of holding a charge of 2,500 gallons, and provided with suitable agitators and either dry or wet steam coils, the bottom of the saturators being connected by three-inch wrought-iron valves and pipes to a powerful pump for the purpose of removing the contents of the saturator when desired. The saturators are grouped together in sets of four for facilitating the lixiviation of the contents by means of repeated washings, after the first decomposition of the mineral. The saturators, as in the case of the manufacture of borax from boracic acid, are first charged with liquor and brought to the boil; a charge of soda ash, usually about 30 cwt., being put in, which is sufficient to decompose three tons of the borate of lime which is gradually added after the soda ash is all dissolved. The soda ash gradually but completely decomposes the sesquiborate without tumult, forming carbonate of lime, borate of soda, and biborate of soda: $Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$.

After boiling five hours the steam and agitators are stopped, and the muddy liquor allowed to settle for ten hours, after which time the clear supernatant liquor is run off to vats to crystallise, and the residue is again washed with weaker liquor from the saturator previously washed, the operation being repeated of boiling and washing with the gradually weaker liquors from the other saturators in rotation. By the time the mud has received eight washings, the last being with water, the whole of the borax will have been removed, and the chalk which is left is then pumped through an iron filter press, which completely presses out the remaining weak liquor and leaves the chalk in a solid cake, which is generally thrown to one side, being too impure for any purpose. The first liquor run to the vats contains the biborate and borate of soda, together with carbonate and sulphate of soda in solution. The biborate of soda or borax crystallises out after cooling in the vats for about six days, leaving the borate of soda in solution. The liquor is then siphoned off into the well and pumped to the boiling-down pans, where it undergoes the process of concentration until it reaches a sp. gr. of 1,350 to 1,400 (70° to 80°Tw.), when it is run off into vats and allowed to throw a further crop of borax. The mother-liquor is now of a syrupy consistence, and is pumped into a decomposing tank, where carbonic acid gas is blown through it. The following decomposition takes place:

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

The borax falls to the bottom of the tank in a finely-divided state, whilst the carbonate of soda remains in solution, and can be used over again in the saturators for the first operation. The refining of the borax from the first process is the same as that employed in the boracic acid process, and therefore need not be further described. The only precaution necessary is the addition of a little bicarbonate of soda in the pans to decompose any borate of soda that might be associated with the borax. Three tons of borate of lime, testing 100 p.c. borax, produce 2 tons of borax and 1 ton borax in the state of borate of soda. Borate of soda may be formed by mixing the concentrated solutions of borax and caustic soda together in their equivalent quantities, and evaporating to 70°Tw.:

$$Na_2B_4O_7 + 2NaHO = 4NaBO_2 + H_2O,$$

from which the borate of soda crystallises in needle-shaped crystals having the formula $NaBO_24H_2O$, and the composition:

Boracic acid	25·3
Soda	22·5
Water	52·2
	100·0

100 parts of borate of soda, when decomposed by carbonic acid, produce 65·6 parts of borax, and 34·4 parts of carbonate of soda; about 30 cwts. of borate of soda then produces 20 cwts. of borax.

Manufacture of borax from ulexite.

Borax is manufactured from this mineral at the various deposits, and also in England, France, and Germany, to which places it is exported from Chili and California, selected and packed in sacks.

The first operation consists in reducing the material to a state of fine division, and for this purpose a mill is used so constructed as to tear the borate to pieces instead of grinding it, which, owing to its fibrous silky nature, is found preferable.

The borate is then mixed with its proper proportion of soda ash and bicarbonate of soda, or soda ash and boracic acid, having regard to the fact that if associated with much gypsum a proportionate additional allowance of soda ash must be made, as the gypsum decomposes the sodium carbonate, forming sodium sulphate and chalk. The composition of ulexite being $Ca_2B_6O_{11}Na_3B_4O_7$, it requires one equivalent of bicarbonate of soda and one equivalent of carbonate of soda to decompose it:

$$2(Ca_2B_6O_{11}Na_2B_4O_7) + 2NaHCO_3 + 2Na_2CO_3 = 5Na_2B_4O_7 + 4CaCO_3 + H_2O.$$

These ingredients are all mixed together in the dry state. The process adopted is similar to the processes already described—namely, that of first boiling the liquor in the saturator, then gradually adding the crude material, boiling, settling, lixiviating.

100 parts of the ulexite, testing 43 p.c. boracic acid, require 10 parts of bicarbonate of soda and 12 parts of carbonate of soda, for its conversion into 117 parts of borax.

Manufacture of borax from crude borax.

This branch of the industry is generally carried on at the borax marsh. It may be desirable to give a description of the Saline Valley, Inyo County, California, where the most extensive deposit of natural borax exists in North America, before entering into the details of refining.

The valley, situated on the eastern slope of the Sierra Nevada Mountains, eleven miles from the Carson and Colorado railroad, is eighteen miles long and twelve miles wide, surrounded with mountainous hills which afford no outlet, and therefore the valley may be said to be the bottom of a dried-up lake. At the point of deepest depression an area of over one thousand acres is covered with crude borax from six to eighteen inches in depth. The colour of the crude material as it lays upon the level plain is of a peculiar gray yellow, giving the surface the appearance of snow somewhat tinged by age. The borax in Saline Valley is mixed with sand, which is volcanic ash and decomposed lime rock, sodium sulphate, sodium carbonate, and sodium chloride. The surrounding hills consist of granite, marble, dolomite, black lava, and felspar. The composition of the crude material varies in strength from 10 p.c. of borax up to 90 p.c., whilst in some places on the marsh under a crust composed of sodium sulphate, sodium carbonate, and common salt, beds of tincal, or large crystals of borax, some two feet in thickness, are found, whilst below the tincal there is a strong saturated yellowish liquor containing one pound of borax to the gallon. All the manipulation that is required is to shovel off the surface of the marsh to a depth of eighteen inches and cart the material to long semicircular wrought-iron pans set on arches of stone, fired beneath with wood fuel obtained in the neighbourhood. The pans are charged with water, and the crude material thrown in and vigorously stirred about with long poles, until, with the aid of heat, all the soluble salts are dissolved. The fires are then withdrawn, and the contents of the pan allowed to settle for ten hours, when the liquor is drawn off into vats, where the borax crystallises out. The mother-liquor after six days is drawn off, and the borax is taken out and packed into sacks for shipment.

Manufacture of boracic acid by sulphurous acid.

This process consists in first of all grinding the borate of lime or ulexite to an impalpable powder.

A large wrought-iron tank, circular in shape and egg-ended, is lined with stout sheet lead; it is provided with a cover and still head, mechanical agitator, and steam pipes. It is first of all charged about half full with water or weak liquor from a previous operation. The liquor is then boiled, and the powdered borate fed in by means of an Archimedean screw.

Sulphur is then burnt in an adjoining furnace, and the sulphurous gas is injected by means of a peculiarly constructed lead injector into the boiling liquor. The gas is wholly absorbed by the calcium borate, which itself is slightly soluble in water, boracic acid and calcium sulphite being formed. The steam arising from the operation, containing boracic acid vapours, passes from the still head through a condenser in order to prevent any loss that would occur. When the operation is complete, the steam and gas are shut off, and the contents of the pan allowed to settle, which occupies about ten hours. The clear boracic acid liquor is then run either into vats made from white sugar pine, or of ordinary wood lead lined, where the boracic acid crystallises out. The mother-liquors are then drawn off, to be used over again if not too highly impregnated with foreign salts, or still further treated for the recovery of the calcium sulphite and the slight percentage of boracic acid they contain.

Boracic acid is also made by treating calcium borate with either muriatic, sulphuric, or acetic acid.

Borax may be determined volumetrically. For this assay, a standard solution of hydrochloric acid is prepared, in which an exact chemical equivalent of the borax shall be contained in each litre. The standard solution preserved in a well-corked bottle provided with a glass siphon tube, is erected on a shelf over the burette, so that the standard solution may be fed into the burette as required. An equivalent of the borax to be assayed (or rather what would be an equivalent if pure) must then be dissolved in distilled water. Now, if both solutions were exact equivalents, they would neutralise one another if poured together. When litmus is added to a solution of borax, only a purple-blue colour is seen while any borax remains undecomposed, but immediately there is the slightest excess of acid a light-red colour appears; if there be any doubt, dip pieces of red and blue litmus paper into the solution and dry them. The standard solution is so regulated that 100 c.c. are equivalent to 10 grms. of borax; if on weighing 10 grms. of the substance to be examined only 80 c.c. are required, the material is 80 p.c. pure. Care must be taken to see that no carbonates or hydrates of other alkalis or alkaline earths are present, or they must be removed by boiling with bicarbonate of soda and precipitation by barium chloride. All borates for the sake of estimation should be converted into borax.

Boracic acid is estimated commercially by what is known as the 'Leghorn test.' Absolute alcohol is prepared by allowing methylated spirit to stand on quicklime, freshly burnt and inclosed in a well-stoppered bottle for two or three days. The alcohol is then distilled off the lime by means of a water-bath, and if not absolute the rectification must be repeated until the alcohol is deprived of all its water. From the sample of commercial boracic acid to be tested 5 grms. are weighed off and placed in a desiccator over the strongest oil of vitriol. The loss sustained after remaining from twenty-four to forty-eight hours is the hygroscopic water; the remainder of the sample is then finely powdered and sifted, and 5 grms. taken and boiled with 50 c.c. pure alcohol, and filtered through a weighed filter of the best Swedish paper (2 inches in diameter), previously carefully dried over oil of vitriol in a desiccator. The residue is again treated with alcohol, and the contents of the beaker poured on to the filter and washed with alcohol until the filtrate shows no traces of a green flame. The filter and its contents are then dried for twenty-four hours in a desiccator over oil of vitriol and then weighed; on subtracting the weight of the filter the quantity of solid matter contained in the boracic acid is obtained. As this consists of sulphates of ammonia, magnesia, soda, iron, and other substances insoluble in alcohol, the loss by difference is the boracic acid less the hygroscopic water, which of course filters through with the boracic acid. In making the test the acid is boiled with the alcohol in the water-bath. The alcohol, contained in a little wash bottle used for washing, is also boiled on the bath to avoid risk of the alcohol igniting. With ordinary care the process is fairly accurate.

Where it becomes necessary to examine for the presence of boracic acid existing in very small quantities, such as in the waters of lakes or oceans or eruptive mud or vapours, by far the best test is that afforded by the direct vision spectroscope, which shows three distinct bands in the green part of the spectrum.

100 parts of boracic acid B_2O_3 are equivalent to 177·1 parts crystallised boracic acid.

100 parts of boracic acid B_2O_3 are equivalent to 272·8 parts crystallised borax.

100 parts crystallised boracic acid B_2O_33aq are equivalent to 154·0 parts crystallised borax.

100 parts calcined borax $Na_2B_4O_7$ are equivalent to 189·0 parts crystallised borax.

Composition of borax minerals.

Formula	100 parts of	Boracic acid, p.c.	Water, p.c.	Soda, p.c.	Lime, p.c.	Commercial article. p.c. substance	= p.c. B_2O_3
$Na_2B_4O_7$.	Calcined borax . .	69·05	—	30·95	—	100	69·05
$Na_2B_4O_710aq$.	Crystallised borax .	36·60	47·2	16·20	—	100	36·60
B_2O_33aq .	Crystallised boracic acid	56·40	43·6	—	—	80	45·70
$Ca_2B_6O_{11}$.	Sesquiborate of lime .	65·20	—	—	34·8	100	65·20
$Ca_2B_6O_{11}5aq$.	Hydrated lime . .	50·90	21·9	—	27·2	80	40·70
$Ca_2B_6O_{11}16aq$ $Na_2B_4O_7$.	Ulexite . . .	43·10	35·4	7·70	13·8	50	21·60

Borax and boracic acid are applied in the manufacturing industries as follows:—

Brick and tile makers. Glazed surfaces.
Candle makers. Preparation of wicks.
Cement. Making the finest kinds, which take a polish.
China and earthenware. In preparing a fret used for glazing what is technically termed 'biscuit ware' in pottery of all descriptions.
Colour makers. In preparing Guignet's green and borate of manganese (a drier).
Coppersmiths. In brazing.
Druggists. Pharmaceutical preparations.
Enamelled iron. An enamelled coating to cast and wrought iron.
Glass. Making pastes and as an ingredient.
Hat makers. Dissolving shellac for a stiffener.
Ironsmiths. In welding.
Jewellers. In soldering. (Ancient name for borax, 'chrysocolla,' gold-glue.)
Laundresses. As a starch-glaze for linen.
Paper makers. Superfine note and highly-glazed paper and cards.
Pork packers. Curing and preserving hams and bacon.
Safe makers. Lining safes to resist fire.
Soap makers. As an emollient.
Tanners. Dressing leather.
Textile manufacturers. Solvent-bleach; mordant; fireproofer.
Timber merchants. In preparation of hard from soft wood.

Production of borax materials.

Turkey in Asia	8,000 tons
India	2,000 „
Italy	3,000 „
United States	6,000 „
Chili and Peru	2,000 „
	21,000 „

Consumption of borax.

Great Britain	5,000 tons
United States	5,000 „
Germany	3,000 „
France	3,000 „
Russia	1,000 „
All other countries	4,000 „
	21,000 „

E. L. F.

Sodium silicates. The fact that silica was soluble in the alkalis was well known to the alchemists, who prepared a solution which was known as 'liquor' or 'oil of flints,' and was considered by some to be the *alkahest* or universal solvent, by exposing a mixture of equal parts of calcined flints and salt of tartar (potassium carbonate) to the damp air of a cellar. The fact that the liquid produced was coagulated by an acid was, together with many other properties of soluble silicates, well known to the alchemists (*v.* Lemery, 'Cours de Chimie,' 1675).

The bodies sold as sodium silicate, soluble glass, or water-glass, vary considerably in composition, according to whether excess of silica or of alkali has been used in their preparation. Silicates of the composition $Na_2O.SiO_2$, $2Na_2O.5SiO_2$, $Na_2O.3SiO_2$, and $Na_2O.4SiO_2$ have, however, been prepared. They have been very fully examined by Ordway (Am. S. [2] 32, 162, 337; 33, 27, 35; and 35, 35, 185).

The body known commercially as *water-glass* or *soluble glass* approximates in composition to the formula $Na_2O.4SiO_2$.

Sodium silicates are prepared commercially by fusing powdered flints, quartz, or infusorial earth with sodium carbonate or oxide, or by boiling the same under pressure with a solution of the carbonate or oxide. Sometimes the carbonate is replaced by sulphate in the dry process. It is usual, when preparing the glass in the dry way, to incorporate a certain proportion of charcoal powder in the mixture, as it appears to assist the reaction by its tendency to reduce the carbonate or sulphate.

On the large scale, the mixture usually employed consists of 22 or 23 lbs. of sodium carbonate, 44 or 45 lbs. of white sand or powdered flints or quartz, prepared by heating to redness, quenching in water, and grinding in a mill, and 3 lbs. of charcoal. The mixture is fused on the bed of a reverberatory furnace for eight or ten hours, after which it is drawn, broken up, and dissolved by prolonged boiling in water. The small proportion of sodium sulphide which is often contained in the fused mass from the reduction of sulphates may be removed by the presence of a little copper scale, copper or oxide, or litharge, in preparing the solution.

About 300 lbs. of solution of 30° to 40° Bé. is obtained from 100 lbs. of the solid.

The wet processes of preparation are largely used on account of the greater uniformity of the product, and the fact that it is at once obtained in solution. In the processes introduced by Kuhlmann and modified by Ransome (Pat. No. 10360, 1844), a solution of 100 lbs. of crystallised sodium carbonate, causticised by lime and measuring about twenty-five gallons, is heated in an iron boiler or digested with 100 lbs. of finely-powdered flints. The digestion is conducted at a pressure of about 60 lbs. with constant agitation, and is continued for from ten to twelve hours until the liquid is almost free from alkaline reaction, as ascertained by withdrawing a small quantity at a try-cock. At the end of that time it is drawn off, strained, and allowed to settle, and the decanted liquid is concentrated to the required strength, usually about 140°Tw. (1·7 sp.gr.) in iron pans.

The presence of earthy oxides in the materials used renders solution increasingly difficult, and adds largely to the amount of insoluble matter produced. Hence the necessity for the use of silica of considerable purity.

A very pure silicate is obtained by passing a current of carbon dioxide gas through the solution of the crude silicate, separating the precipitated gelatinous silica, and re-dissolving it in caustic soda.

The aqueous solution of 140°Tw. usually has the following composition: Silica, 32 to 33 p.c.; soda, 16 to 16·5 p.c.; other sodium salts, 2·5 to 3 p.c.; water, 48 to 49 p.c.

A water-glass known as 'double soluble glass,' and containing about equal proportions of sodium and potassium silicate, is prepared by the use of proper proportions of potassium and sodium carbonate. It is said to give a thinner solution than either the potassium or sodium silicate of corresponding strength, and is preferred for some purposes. Ordinary water-glass is nearly insoluble in cold water, but dissolves almost completely, though slowly, in boiling water. Its solubility decreases as the percentage of silica increases. Silicates which contain more alkali than corresponds with the composition $Na_2O2\frac{1}{4}SiO_2$ are deliquescent, and too poor in silica to be applicable for the ordinary uses of water-glass (Ordway, Am. S. [2] 35, 193). The alkalinity of the solution may be reduced by the addition of a mineral acid.

For the purposes of the soap-maker, the solution should contain at least twice as much silica as soda.

Among the patents taken out for the manufacture of water-glass reference may be especially directed to those of Ransome: No. 10360, 1844; 10665, 1845; 1666, 1853; 645, 1855; and 2267, 1856. Kuhlmann: 367, 1853. Losh: 14208, 1852. Gossage: 762, 1854; 799, 1859; 1099, 1859.

Alcohol precipitates sodium silicate, even from a weak solution; but the precipitate contains an increased proportion of silica, while the solution retains a small quantity of a more alkaline silicate. When treated with acids (even carbonic acid) the salt is entirely, though sometimes gradually, decomposed, with precipitation of gelatinous silica. The alkaline carbonates and chlorides, especially ammonium chloride, also precipitate the silica; and the oxides and most of the soluble salts of barium, calcium, strontium, and aluminium precipitate the bulk of the silica, and a proportion of the alkali, in the form of double silicate.

Water-glass is largely used, on account of its detergent properties, as an addition to soap, as in Gossage's well-known 'silicated soap.' It is also used in dyeing and calico-printing, as a 'fixing' agent for ultramarine blue and other pigments; as a substitute for borax in dyeing certain blues and greens; and, under the name 'dunging salt,' as a substitute for cow's dung. It is also used in fixing fresco-painting (stereochromy), for rendering wood, paper, &c., uninflammable (Fuchs, S. 24, 378), to prevent the rotting of wood, and for mending stone, &c. Fletcher recommends the use of a pasty mixture of the liquid silicate and ordinary fireclay for repairing furnaces.

An important application of water-glass is for impregnating stone, and for cementing together sand, &c., in the manufacture of grindstones, building stones, &c.

The silicate appears to have been first used by Kuhlmann for hardening chalk and porous stone, the treatment consisting merely in a superficial application of the liquid; but his process was soon superseded by that of Ransome, who followed the treatment with silicate by the application of calcium chloride, which produces a precipitation of calcium silicate in the interstices of the material. This silicate acts as a valuable binding material, and much increases the density and impermeability of the stone, the sodium chloride formed by the reaction being readily removed by a subsequent washing. Ferric chloride has been used instead of the calcium salt.

It is stated that this method of treatment is especially applicable to magnesium limestones, but most porous stones, such as ordinary limestones, sandstones, and even bricks seem to be improved by it.

The following process is employed at a large works in the North of England for the manufacture of grindstones, chimney-pots, mouldings, cornices, mantelpieces, &c. The sand or sandstone having been ground wet and passed through a 40-mesh sieve, is thoroughly dried, and is mixed in a revolving pan provided with scrapers and edge mixers, with sufficient liquid water-glass to form a moist coherent mass.

It is then rammed into moulds, and is saturated before removal with a solution of calcium chloride, prepared by running hydrochloric acid over calcspar, and drawn through by a vacuum equal to about 20″ of mercury. Calcium silicate having thus been formed as above, the stones, &c., are transferred to boiling tanks heated by steam, and, after a sufficient time to complete the setting, are conveyed to washing tanks, in which they are subjected to the action of running water for a fortnight, to remove the whole of the sodium chloride.

For further information regarding the use of sodium silicate for preserving stone, &c., reference may be made to the above list of patents, and to a lecture by Burnell (J. Soc. Arts, 8, 240).

SOFT CEMENTS *v.* LUTES.

SOLANINE *v.* VEGETO-ALKALOIDS.

SOLAR STEARIN *v.* STEARIN.

SOLDERS. Solders consist of fusible alloys, which are used for joining metals together, and are of various kinds, depending upon the nature of the metals to be joined. They are distinguished by specific names, as hard-, soft-, white-, spelter-, silver-, gold-, aluminium-, copper-, tin-, plumbers'-, pewterers'-, and button- solder, &c., but for whatever purposes they may be intended they should always be rather more fusible than the metal or metals to be united; and, to give the maximum strength, they should have about the same hardness and malleability as these metals. Hard solders require a red heat to fuse them, and they are used to join the more refractory of the metals, in which process a forge or a blast blowpipe is required; whereas some of the soft solders melt even below 100°C., and by varying the proportions of the constituents they may be made, within certain limits, to melt at any desired temperature, thus admitting of various applications for electrical and other purposes. A few examples of such are shown in the accompanying table:—

Bismuth solder.

Parts of tin	Parts of lead	Parts of bismuth	Fusing-point
3	5	3	94·4°C.
2	2	1	109·4°C.
2	1	2	113·3°C.
1	1	1	123·3°C.
3	3	1	154·4°C.
4	4	1	160°C.

Soft solders can be applied by a soldering iron—that is, a copper bit, or a plumbers' iron, and they generally melt below 300°C. The following table exhibits the varying point of fusion for different proportions of the ingredients taken in a number of soft solders (Tomlinson):—

No.	Tin	Lead	Melting-point	No.	Tin	Lead	Melting-point
1	1	25	292°	7	1½	1	168°
2	1	10	283°	8	2	1	171°
3	1	5	266°	9	3	1	180°
4	1	3	250°	10	4	1	185°
5	1	2	227°	11	5	1	192°
6	1	1	188°	12	6	1	194°

Almost all the well-known more fusible metals are employed in the preparation of solders, and the majority of the metals can be joined by one or other of these solders. An important point to be observed in preparing solders is that they should be well stirred before pouring, preferably with a piece of green wood, and the surface of molten metal should be exposed as little as possible to the air, so that oxide shall not form on the surface. To prevent the formation of oxide a good plan is to cover the molten metal with bits of charcoal. One of the conditions of a good solder is that it should run easily when melted; hence it is necessary that one of the constituents of the solder should be the same as that of the metal to be soldered, or be a metal which will readily alloy with it.

The finer kinds of solder are cast into sticks or drawn into wire, while the harder kinds are generally prepared in irregular masses or grains. Recently, however, solders have been made in the form of a narrow bore-tube, with the central portion filled up with rosin or other material, so as to obviate the necessity of using a separate 'flux.'

The kind of 'flux' is varied with the work to be done: *e.g.* for *lead*, tallow or resin is employed; for *lead* and *tin pipes* and *pewter*, resin and sweet oil; for *copper*, *gun-metal*, *brass*, *silver*, &c., borax or zinc chloride; for *zinc*, hydrochloric acid; for *iron* or *steel*, borax or sal-ammoniac; for *tinned iron*, resin or zinc chloride; and so on. The composition of a number of solders is as follows:—

For *Pewter*, *Britannia metal*, &c. 10 parts of tin, 5 lead, and 1 to 3 of bismuth.

For *Lead* and *Zinc*. 2 parts lead and 1 part tin.

Plumbers' coarse solder. 1 part tin and 3 parts lead; melts at 250°. *Plumbers' fine solder.* 1 part tin and 2 parts lead; melts at 227°.

Tinned iron. 7 parts of lead and 1 of tin.

Tinman's coarse solder. 3 parts tin and 2 of lead; melts at 168°. *Tinman's fine solder.* 2 parts tin and 1 of lead; melts at 171°.

White or *button solder.* 10 parts tin, 6 copper, and 4 brass; or 10 copper, 8 brass, and 12 zinc.

Copper, *iron*, and *dark brass.* Equal parts of copper and zinc are melted together; but for pale brass a larger proportion of zinc is used.

Steel. 19 parts silver, 3 copper, and 1 of zinc.

Black solder. Two lbs. of copper, 3 lbs. of zinc, and 2 ozs. of tin.

Hard solder. 86·5 parts of copper, 9·5 zinc, and 4 of tin.

Middling-hard solder. 4 parts of the metal to be soldered and 1 part of zinc.

For sealing iron in stone. 2 parts of lead and 1 of zinc.

For sealing tops of canned goods. 1¼ lbs. of lead, 2 lbs. tin, and 2 ozs. of bismuth.

German silver solder. 5 parts of German silver and 4 of zinc melted together, run into thin flakes, and then powdered.

Aluminium solder. 55 parts tin, 23 zinc, 5 silver, and 2 parts aluminium. No flux is required (S. C. I. [5] 431).

Other aluminium solders are: 89·5 zinc, 4·5 copper, and 6 parts aluminium; or 9 zinc, 18 tin, 3 copper, 3 silver, and 6 parts aluminium. A soft solder for aluminium consists of 94 parts of tin and 6 of bismuth.

Silver solder. 1 part silver, 8 copper, and 8 zinc. Used for fine bronze, gun-metal, and brasswork; for German silver, fine bronze, and gun-metal equal parts of silver, zinc, and brass may be taken, or 6 parts of fine brass, 5 silver, and 2 of zinc.

Soft silver solder. 2 parts of fine silver, 1 brass wire, and ¾ part arsenic. The latter is added to make the alloy whiter, and to obtain greater fluidity when fused.

Hard silver solder. (1) 4 parts of silver and 1 of copper; (2) equal parts of copper and of coin silver.

Gold solder. 3 parts of gold, 2 silver, 1½ copper, and ½ zinc. *Fine gold solder* consists of 12 parts of gold, 2 silver, and 4 copper. A still finer solder is as follows: 24 parts gold, 2 silver, and 1 copper. These are used by jewellers in making and repairing small articles. Or 12 parts gold, 4 copper, and 2 of silver.

Hard solder for gold. 18 parts of 18-carat gold, 10 silver, and 10 copper.

Platinum. Fine gold, laminated and cut into shreds, is employed for soldering platinum articles and for gold alloys. It gives a very infusible joint, which is not easily attacked by the majority of chemical agents.

Chemical solder. Tinfoil, cut to the size of the joint to be made, is painted over with a solution of sal-ammoniac, then placed between the two portions to be soldered together, and heated upon hot iron, or over a spirit lamp, till the solder melts, the pieces being held together by the hand during the operation. On cooling, a firm joint is the result. This method is very useful for the soldering of small articles together without a soldering iron—*e.g.* pieces of brass or copper wire, the ends of which should first be filed flat.

In the practical application of solders in the joining of metals it is necessary that the surfaces of the metals to be united be bright, smooth, and free from oxides. The contact of the air should be as far as possible excluded during the operation, because one or other of the surfaces would otherwise be liable to oxidise, and thus prevent the formation of an alloy at the point of junction. The autogenous method of soldering which takes place by the fusion of the two edges of metal themselves without the interposition of a metallic alloy as a bond of union is of especial advantage in chemical works for joining the edges of sheet lead used for the manufacture of sulphuric acid chambers and concentration pans, because any solder containing tin, zinc, &c., would soon corrode. The soldering is effected by directing a jet of burning hydrogen, or a jet of coal-gas mixed with air, upon the two surfaces or edges to be joined together. The joints thus made are much less liable to rupture when submitted to varying temperatures, &c., than when the common soldering process is employed.

SOLFERINO. A variety of fuchsin. *V.* TRIPHENYL-METHANE COLOURING MATTERS.

SOLIDE JAUNE *v.* AZO- COLOURING MATTERS.

SOLID GREEN (*Alsace green*, *Resorcinol green*) is the iron salt of dinitrosoresorcinol $C_6H_2O_2(N.OH)_2$ [O:N.OH:O:N.OH 1:2:3:4 (Kostanecki, B. 20, 3137)].

Dinitrosoresorcinol is prepared by adding an aqueous solution of sodium nitrite (2 mol. prop.) to a solution of resorcinol (1 mol. prop.) in 50 times its weight of water cooled at 0°, and acidified with acetic acid (2 mol. prop.). The liquid rapidly becomes dark in colour, and a greenish-coloured substance, consisting of dinitrosoresorcinol and its acid sodium salt, separates from the solution. After standing for some time, dilute sulphuric acid (2 mol. prop.) is added to the product, and dinitrosoresorcinol separates in a yellow flocculent form. The yield amounts to about 80 p.c. of the theoretical when the preparation is carried out rapidly and at a low temperature (Fitz, B. 8, 631).

Commercially, dinitrosoresorcinol is met with as a greyish-brown powder. It crystallises from hot water or dilute alcohol in yellowish-grey or yellowish-brown scales of the composition $C_6H_4N_2O_4 + H_2O$ (Kostanecki, B. 22, 1345), and is insoluble in benzene and ether; the hot solutions rapidly become brown on exposure to the air. When heated at 115° it explodes. Treatment with even dilute nitric acid converts it into styphnic acid (Fitz, *l.c.*; Kostanecki, B. 22, 3120). It expels carbon dioxide from carbonates, and forms a series of salts which, with the exception of those of the alkali metals, are amorphous and very sparingly soluble in water. Like orthoquinonoximes generally (*cf.* Kostanecki, B. 20, 3146), it possesses tinctorial powers, and with iron mordants gives on cotton a beautiful dark-green colour, fast alike to soap and light, whilst with cobalt and nickel sulphates as mordants it yields fast shades of chocolate and yellowish-brown respectively (*cf.* Ulrich, S. C. I. 9, 1127).

See also *Malachite green*, art. TRIPHENYL-METHANE COLOURING MATTERS.

SOLUTION. A solution is a homogeneous liquid consisting of a liquid (the solvent) and another substance, which may be a gas, a liquid, or a solid.

From time to time various hypotheses have been brought forward to account for the solubility of a substance in a liquid. These may be divided into two classes, chemical and physical, according to the explanation that they give of the constitution of a solution. For an account of these several hypotheses reference must be made to the original papers, the more important of which are as follows:

Chemical.

1. Berthollet, 1801, Statique Chimique.
2. Persoz, 1837, A. 23, 80.
3. Berthelot, 1872, A. Ch. [4] 26, 433.
4. Berthelot, Mécanique Chimique [2] 160.
5. Pickering, 1886, Atomic Valency (pamphlet).
6. Pickering, 1886, C. N. [54].
7. Pickering, 1887, C. J. 51, 593.
8. Pickering, 1890, B. A. Report, Leeds.

Physical.

9. Dossios, 1867, J. 92.
10. Nicol, 1883, P. M. 91.
11. Tilden and Shenstone, 1884, Tr. part I. 23.
12. Nicol, 1885, B. 18, 149.

A solution differs from ordinary chemical compounds in several well-marked points, resembling more a partially or completely dissociated compound, for in solutions the state of equilibrium between the solvent and the substance dissolved is exceedingly unstable, a slight alteration of temperature or an increase of pressure being sufficient to alter the proportions of the two substances.

THE PHENOMENA OF SOLUTION.

The solubility of gases in liquids.

13. Henry, 1803, Tr.
14. Dalton, 1807, Mem. Lit. and Phil. Soc. Manchester [1].
15. Bunsen, 1855, A. 93, 1.
16. Roscoe and Dittmar, 1860, C. J. 12, 128.
17. Setschenow, Mem. d. Petersburg, 22, 1.
18. Mackenzie and Nicholls, 1878, W. 3, 134.
19. Wiedemann, Handwörterb. d. Chemie, Ladenburg, 1, 4.
20. Sims, 1862, C. J. 14, 1.
21. Thomsen, Thermochem. Untersuch. [2].
22. Timoféef, 1890, Zeit. Phys. Ch. 6, 141.
23. Winkler, 1891, B. 24, 89.
24. Ångström, 1882, W. 15, 297; 1887, W. 33, 223.
25. Winkler, 1892, Zeit. Phys. Ch. 9, 171.

All gases are soluble to some extent in water and other liquids. The solubility in water is subject to the following laws:—

Connection of solubility with the temperature.

The solubility (absorption coefficient) is in so far dependent on the temperature that it is smaller the higher the temperature. For supposed exceptions consult Bunsen (15), also (22), (23). Wiedemann (19) has recently pointed out that in the case of water as a solvent the decrease of solubility of a gas is approximately proportional to the rise of temperature. All gases, therefore, with a few exceptions to be noted afterwards, are completely expelled from solution by boiling. For temperature effect on solubility of gases *v.* Winkler, Zeits. f. Physik. Chemie, 1892. Ångström has made special observations on this point (*v.* W. 15, 397; 33, 223).

Connection of solubility with the pressure.

In 1803 Henry (13) pointed out that when the temperature is constant the weight dissolved of any gas is directly proportional to the pressure (Henry's law). From this it follows, by

Boyle's law, that the volume dissolved of any gas is a constant, no matter what may be the pressure, provided, of course, that excess of gas be present. This law has since been verified by Bunsen (15), who found that it held good under very varying pressures for all but the very soluble gases, such as ammonia, which are also exceptions to Boyle's law at low temperatures. If, however, the experiments be performed at higher temperatures, then the exceptions to a great extent disappear. In 1807, Dalton (14) showed that Henry's law is applicable to mixtures of gases. Each constituent gas dissolves in the liquid in direct proportion to the pressure which it exercises in the gaseous mixture. (Sims (20) has shown that a few mixtures of gases, the constituents of which individually obey Henry's law—*e.g.* hydrogen and chlorine—are exceptions to the above.)

Hence to calculate the solubility of a mixture of two gases A and B at pressure P, where a and b are the solubilities of the two gases separately at that pressure, and p and p' the percentages of the respective gases in the mixture; we have

$$\frac{ap}{100} = \text{amount of A, and } \frac{bp'}{100} = \text{the amount of B.}$$

From Henry's law it follows that any gas can be completely expelled from solution by reducing the pressure to zero, and from Dalton's law it is evident that the end may be attained by passing an excess of another gas through the liquid. To both these, however, there are noteworthy and important exceptions. Thus hydrochloric acid gas (16) dissolves in water at 20°C. to form a solution which contains 41·89 p.c. of the gas. If this solution be heated it loses gas and becomes weaker, while if, say, a 10 p.c. solution be heated it loses water, and becomes stronger, till in both cases the boiling-point becomes constant at 110°C. at 760 mm., and both solutions distil over without further change of composition, and the distillates and liquids in the retort are found to contain 20·24 p.c. of the gas. If, however, the distillation be conducted under another pressure, the percentage of gas in the acid of constant boiling-point rises with decrease of pressure and *vice versâ*. The same holds good for the solution obtained by passing dry air through a weak or strong solution of the gas: the strength of the solution is the same as that of one which boils at the temperature of experiment.

The solubility of gases in other liquids than water has been but little examined. Bunsen (15) has made many determinations for alcohol, while the solubility of carbon dioxide in salt solutions has been partially studied by Mackenzie and Nichols (18) and Setschenow (17). The results, however, are far from complete, and are of little general interest.

When a gas dissolves in a liquid the density of the latter is always altered (24). Generally, it is increased, as is the case with hydrochloric acid and sulphurous acid. Sometimes it is diminished, as, for instance, ammonia. The diminution of volume undergone by the gas is, in the case of the more soluble gases, extremely great, and equal to that produced by the pressure of many atmospheres. Thus a saturated solution of ammonia at 0°C. and 760 mm. contains an amount of gas condensed into such a volume as would, if effected by pressure alone, require over 500 atmospheres, or about 3½ tons per square inch. Of course the gas would be liquefied ere this pressure was reached.

The act of solution of a gas in water is attended in general by evolution of heat, which with the more soluble gases is often very considerable. Thus Thomsen (21) gives the thermal change when a gram-molecule of each of the following gases is dissolved in large excess of water as:

Ammonia	8435 calories
Hydrochloric acid	17314 „
Carbon dioxide	5880 „

The solubility of liquids in liquids.

26. Dupré, 1872, Pr. 20, 336.
27. Bussy et Buignet, 1865, A. Ch. [4] 4, 5.
28. Alexejeff, 1875, B. 265; 1876, B. 1442 and 1810; 1879, B. 2, 172.
29. Konovalow, 1881, W. 14, 34.
30. Mendeléeff, 1869, P. 138, 103 and 230; 1886, B. 19, 400; C. J. 1887, 778.
31. Pickering, 1890, C. J. 57, 64 and 331.
32. Lunge, 1884, B. 1748 and 2711.
33. Gilpin, 1792–94, Tr. 1792, 439; 1794, 275.
34. Ure, 1822, Schweigger's Journ. 35, 444.
35. Fownes, 1847, Tr. part 1, 25.
36. Oudemans, 1866, J. 300.
37. Handwörterb. d. Chemie, 1882, Ladenburg [1] 457, 464.
38. Emo, 1882, W. Beibl. 6, 662.
39. Nicol, 1887, Ph. 17, 302.

Here there are two phases:

1. Miscibility in all proportions, as alcohol in water.

2. Limited solubility, generally mutual, as ether in water.

References to the more important instances will suffice for the liquids belonging to Class I. These are also the more technically important cases.

Sulphuric acid and water (30), (31), (32).
Alcohol and water (30), (33), (34), (35), (37).
Acetic acid and water (36).
Glycerin and water (38), (39).

For information as to examples of Class 2 reference may be made to (27) and (28), while attempts at ascertaining the laws affecting the solubility of liquids and the boiling-points of such solutions and their behaviour on distillation are to be found in the papers of Dupré (26), and especially Konovalow (29).

The solubility of solids in liquids.

This subdivision of the wide subject of solution is at once one of the most important and the most generally experimented on, though it is greatly to be regretted that the vast majority of the determinations are but of little value, owing to neglect of the conditions necessary to insure accuracy of results.

Nearly the whole of our knowledge of this branch is confined to the solubility of salts in water and to the physical properties of the resulting solutions, and the following remarks must be held to apply to such solutions except where otherwise stated.

The extent to which a salt dissolves in water is dependent, first on the nature of the salt, second on the temperature of the water, and third on the pressure, though this last is but of small influence.

40. Mulder, 1864, Bijdragen tot de Geschiedenis van het Scheikundig Gebonden Water.
41. Poggiale, 1843, A. Ch. [3] 8, 463.
42. Gay-Lussac, 1819, A. Ch. 11, 296.
43. Tobler, 1855, A. 95, 193.
44. Etard, 1884, C. R. 98, 993 and 1276; 1888, C. R. 106, 206 and 740, &c.
45. Marignac, 1874, A. Ch. 15, 279.
46. Sorby, 1862, Pr. 12, 544.
47. Alexejeff, 1887, W. 28, 305.
48. Carnelley and Thomson, 1888, C. J. 53, 782.
49. Handwörterb. d. Chemie, Ladenburg [6] 527.
50. de Coppet, 1883, A. Ch. [5] 30, 411.
51. Nicol, 1884, P. M. 537.
52. Tilden, 1886, B. A. Report, Birmingham.

The nature of the salt appears to be of paramount importance in determining the amount dissolved. The solubility varies greatly, from barium sulphate, soluble in 250,000 parts of water, to such salts as sodium thiosulphate, which at 45°C. is soluble in all proportions in water. Little or nothing is known as to the laws governing the solubility or insolubility of a salt. In a few cases, it is true, faint traces of underlying general laws have been observed. Thus for salts of the same type—the sulphates for example—those of metals of the same group are sometimes, as is the case with the metals of the alkaline earths, more soluble the smaller the atomic weight of the metal. The same is true of the chlorides and nitrates of potassium and sodium, but only at the ordinary temperature; a rise of temperature suffices to reverse the position of the two. Other qualitative, rather than quantitative, relations have been observed; compare Mulder (40). Mulder has made the following general observations as to the causes which affect the solubility of a solid:—

'Solubility is increased by the addition of oxygen, hydrogen or chlorine to an element, and in the case of compounds the increase in the number of halogen atoms is accompanied by increase of solubility.

'The solubility of a salt is dependent on both the metal and salt radicle, and is in no way connected with the rapidity with which solution takes place.

'Anhydrous salts are not generally less soluble than hydrated salts.'

These generalisations will, on reflection, show clearly by their incompleteness and limited applicability how little is really known of the cause of solubility or otherwise of a solid.

Determination of solubility (49). The innumerable determinations of solubility scattered throughout the scientific journals are too often found to be completely inaccurate. Experience has shown that solubility determinations require the greatest care, and that, in addition, the following conditions must be observed to insure success.

The salt must be of the very highest degree of purity obtainable, otherwise the traces of foreign bodies present dissolve out of the excess of salt present, and unduly raise the result (51).

Excess of solid salt must be present throughout the experiment.

The determination must be made, starting with cold water, which is heated up to and never above the temperature of experiment, unless the duration of the experiment is unduly prolonged.

Once the temperature of experiment is reached it must be kept constant, and the solution must be inclosed, so that evaporation is impossible. The solid and solvent must be constantly agitated.

The time of experiment should be at least six hours, better twenty-four, and the taking of, and weighing, the sample of the saturated solution should be performed as rapidly as possible.

When all these conditions are carefully observed there is little danger of supersaturation, and if the other operations are skilfully performed the results will be accurate.

It is highly desirable that some uniform temperature should be fixed on for single determinations, and that for the sake of convenience a uniform system of expressing the result should be adopted. The temperature of 20°C. and S. = solubility in parts of solid to the 100 parts of solvent by weight, will, it is believed, meet with general approval.

Effect of temperature on solubility. Rise of temperature usually increases the solubility of a solid. Sometimes, but rarely, it is without effect, but in a number of cases the solubility is diminished.

Typical examples of each of these effects of rise of temperature are:—

Potassium nitrate S. at 0° = 13·3; S. at 100°C. = 247.

Sodium chloride S. at 0° = 35·7; S. at 100°C. = 39·8.

Sodium sulphate S. at 33°C. = 50·6; S. at 100°C. 42·5.

Decreased solubility accompanying rise of temperature is the only phase calling for special notice. The following is a fairly complete list of the salts exhibiting this anomalous behaviour.

Salts which behave normally up to a certain temperature where the maximum solubility is attained are:—

Calcium sulphate 35°C.
Sodium carbonate 32·5°C. (40).
Sodium sulphate 32·75°C. (40).
Manganese sulphate 54°C.
Ferrous sulphate 63·5°C.

In the case of manganese sulphate the maximum is reached at 54°C. The solubility then decreases, becomes constant at 63·5°, and remains so to 84°; from this temperature it again diminishes up to the boiling-point of the solution. Tilden and Shenstone have shown that the solubility of sodium sulphate reaches a minimum at 120°C., and from that temperature up to 230°C., the limit of their experiments, the solubility again increases. Sodium selenate, chromate, and molybdate behave in the same way as the sulphate.

Salts, the solubility of which steadily diminishes as the temperature rises, are:—

Strontium sulphate.
Calcium hydroxide.

While many calcium, zinc, and barium salts of organic acids exhibit irregularities in solubility according to numerous observers (49).

Closely connected with the effect of rise of temperature on the solubility of a substance is the melting-point of that substance. When the melting-point of the solid lies within the limits of temperature within which the solubility can be accurately determined, one would naturally expect to find the solubility abruptly altered at the temperature of the melting-point. This, however, is not usually the case; there is no abrupt change observed. Alexejeff (47) has, on the other hand, shown that for such substances there are two solubilities—one for the solid, the other for the melted substance.

Several attempts have been made to definitely connect ready solubility with low melting-point. The most successful of these are those of Tilden and Shenstone (11), and of Carnelley and Thomson (48).

The former experimenters worked with inorganic bodies and carried the solubility curves to 230°C., far above the boiling-points of the saturated solutions, while the latter experimented with isomeric organic substances, and found that for pairs of isomers lower melting-point is accompanied by greater solubility; and that the ratio of the solubilities of two isomers is independent of the nature of the solvent.

The physical properties of salt solutions. When a liquid contains a dissolved solid the physical properties of the resulting solution differ from those of the pure solvent to an extent which varies with the nature of the solid and the amount of it present in the solution. Very many of the physical properties of salt and other solutions have been thoroughly and exhaustively studied; others, again, such as the freezing-points and the electrical conductivity, have come to the front comparatively recently, but all as yet are far from being thoroughly understood, and shown to conform to really general laws. In this place, however, little more can be done than to give the more important results of the successful workers on the subject, with copious references to the papers containing these results and deductions therefrom; and in this the arrangement adopted by the committee of the British Association for the Advancement of Science, on the bibliography of solution, will be followed.

1. *The density of solutions.*

53. Gerlach, 1859, Spec. Gewichte der Salzlösungen, Freiberg.
54. Kremers, 1854, P. 92, 497; 1855, 94, 87, 255.
55. Schiff, 1859, A. 109, 330.
56. Marignac, 1871, Arch. de phys. Geneva, 42, 92.
57. Thomsen, 1882, Thermochem. Untersuch. [1].
58. Macgregor, 1884–6, Trans. Roy. Soc. Canada [3], 64; Proc. Nova Scotia Inst. 6, 261.
59. Nicol, P. M., 1883, 121; 1884, 150, 179.
60. Favre et Valson, 1871, C. R. 73, 441.
61. Bender, 1883, W. 20, 574.
62. Ostwald, 1878, Kolbe's Journ. 18, 353.

The sp.gr. of a solution is rarely, if ever, calculable from the sp.grs. of the solvent and the solid. In general, contraction accompanies the act of solution, and, as a consequence, the sp.gr. of the solution is greater than the calculated. Only a few exceptions to this rule are known, *e.g.* magnesium chloride (Gerlach) (53), and certain ammonium salts (Nicol) (59); in these expansion ensues on solution. The amount of contraction is very varied, and is less per unit of salt the greater the amount dissolved. Thus it follows that while the sp.gr. of a solution increases as the amount of dissolved solid increases, it does so at a rapidly decreasing rate, so that in all probability there is but little contraction on the solution of the last particle in a saturated solution. It is often stated that the strength of a solution is directly proportional to the sp.gr., but such statements will in all probability be found, when the special cases to which they refer are carefully examined, to be due to defective observation. In all well-examined cases the sp.gr. has been found to be a parabola or hyperbola when plotted against the concentration (Mendeléeff).

In the case of some anhydrous salts and other bodies, such as caustic soda, the contraction in dilute solution is so great that the volume of the solution is not only less than the calculated, but actually less than the volume occupied by the solvent before solution (Macgregor) (58), (Thomsen) (57). In some few cases, *e.g.* tartaric acid, the volume change alters its sign in strong solutions.

Closely connected with the sp.gr. of a solution is the molecular volume $M.V = \frac{M.W}{\delta}$. Where $M.W$ = molecular weight of the solution, and d its sp.gr. The molecular volume is thus the reciprocal of the sp.gr. multiplied by the molecular weight, this last being usually expressed in molecules of solid to the 100 molecules of the solvent. The use of the molecular volume enables one to trace out relations not easily detected when the sp.gr. is the form of statement. The importance of this mode of expression was first pointed out by Thomsen (57), and it has become extensively used by Mendeléeff and Nicol (59).

Favre and Valson (60) first showed that for dilute solutions containing one gram-molecule of the salt to the litre of water, the difference between the sp.grs. of such solutions of any two salts of different metals with the same acid radicle is a constant, no matter what may be the acid, and that the same holds good for any two acid radicles, whatever may be the metal with which they may be combined. Thus, according to these experimenters, the sp.gr. of a solution is made up of two factors—one due to the metal, the other to the acid radicle. These factors they called 'moduli.'

This first rough indication of a law was supported by Ostwald's (62) 'Researches on the Volume Change on Neutralisation,' and further by the work of Bender (61), while in 1883 Nicol (59) had arrived at a similar result by observations on the molecular volume, the chief result of his work being that the molecular volume of a salt in solution is made up of two parts, one due to the metal, and the other to the acid radicle; and that these are independent of the way in which they are combined, provided always that the solutions be sufficiently dilute.

The sp.gr. of a solution is a ready, and fairly accurate, means of determining the amount of dissolved salt when only one substance is present, but it is useless for mixtures.

2. *The dilatation of solutions.*

63. De Heen, 1883, Physique Comparée, Brussels.
64. Nicol, 1887, P. M. 385.
65. Tait, Challenger Reports, 1888, Physics [2].

The expansion of salt solutions is the more uniform the more concentrated the solution—that is, the volume curve approaches more nearly to a straight line the stronger the solution. In all cases it is less curved than the volume curve of water. From this it follows that solutions expand more than water at low temperatures, but that at higher temperatures the rate of expansion is less. So marked is this that at temperatures below 100°C. the difference between the volumes of water and a salt solution often actually changes its sign.

It is therefore possible to find for every solution a temperature at which its co-efficient of expansion is the same as that of water at the same temperature. This temperature is, according to de Heen (63), a constant for all solutions of the same salt, whatever may be their concentration, but Kremers (54) holds that this last has a slight effect.

Finally, the rate of expansion of a solution cannot be calculated from the rates of expansion of a weaker and a stronger solution, nor from those of the solvent and solid separate. The maximum density-point of water is lowered by the presence of salt to a greater extent than the freezing-point, consequently moderately concentrated solutions have no maximum density point (Tait, 65).

3. *The freezing-points of solutions.*

66. Rossetti, 1870, 140, 320.
67. De Coppet, 1871–2; A. Ch. [4] 23, 366; 25, 502.
68. Rüdorff, 1861, P. 114, 63; 116, 55; 1871, 145, 599.
69. Raoult. See list given in (45), [6] 587.
70. Ostwald, 1890, Outlines of General Chemistry,' 136.

Blagden in 1788 showed that the lowering of the freezing-point when a salt is dissolved in water is proportional to the amount of dissolved salt. This was re-discovered by Rüdorff (68), in 1861, and in 1871 de Coppet (67) extended the law in so far that he found that similar substances added in molecular proportions to water brought about the same amount of depression of the freezing-point.

In 1882 Raoult (69), as the result of experiments on the freezing-points of aqueous solutions of organic bodies, put forward the law that dilute equimolecular solutions have the same freezing-point, and it was further found that this holds good for other solvents.

If Δ be the depression of the freezing-point caused by n times the molecular weight of the solid in g grms. of the solvent, then $\Delta = r\frac{n}{g}$ where r is a constant depending on the nature of the solvent. This is true only for indifferent substances; salts, strong acids, and bases form exceptions. Taking advantage of this law it is possible to determine the molecular weight of a substance, thus: p grms. of the solid are dissolved in g grms. of the solvent, then $n = \frac{p}{\text{mol. wt.}}$ and $\Delta = \frac{rp}{\text{mw}\,.\,g}$ and $\text{mw} = \frac{rp}{\Delta g}$ r for the solvent in question having been found by dissolving substances of known molecular weight, $r = \frac{\Delta g}{n}$. See Ostwald (70) for an excellent summary of the results hitherto obtained.

4. *Vapour pressures and boiling-points of salt solutions.*

71. Wüllner, 1858-60, P. 103, 529; 105, 85; 110, 564.
72. Moser, 1881, W. 14, 62.
73. Magnus, 1844, P. 61, 225.
74. Von Babo, 1847, Naturforsch. Gesel. Freiburg, 17–18.
75. Legrand, 1835, A. Ch. 59, 423.
76. Konovalow, 1881, W. 14, 51.
77. Tammann, 1885, W. 24, 523; 1887, 29, 165.
78. Nicol, 1884, P. M. 364; 1886, 502.

When a non-volatile solid is dissolved in a liquid the vapour pressure of the liquid is diminished to an extent in some degree proportional to the amount of solid present.

Legrand (75) in 1835 was the first experimenter in this field whose work was at all extensive. He determined the boiling-points at atmospheric pressure of salt solutions of various strengths. His work was followed by that of Wüllner (71), which was much more accurate and extended. More recently the whole question has been exhaustively studied by Tammann (77).

Connected with this is the work of Magnus (73), who, in 1844, found that on passing steam into a strong solution of a salt the temperature of the latter can be raised above 100°C., to the boiling-point of the dilute solution thus obtained.

The diminution of the vapour pressure of a liquid by a dissolved solid is connected with the temperature and concentration, thus:—

(1) The alteration of the vapour pressure of a solution by alteration of temperature is proportional to the alteration in the vapour pressure of pure water by the same temperature change—Von Babo (74).

(2) The diminution of the vapour pressure of water is directly proportional to the amount of dissolved salt—Wüllner (71).

The truth of these two statements is called in question by Tammann (77) and Nicol (78), who have found that though they hold for solutions of low concentration and differing little from one another, they do not apply to strong and widely-different solutions. The molecular diminution of the vapour pressure is rarely a constant, generally an amount which either increases or decreases with the concentration.

Raoult (69) has recently examined the molecular diminution of vapour pressure for solutions of organic bodies in various solvents, and finds that for ethereal solutions and for a limited temperature range it is a constant, independent of the nature and amount of the dissolved body. With other solvents the value of the constant is often doubled:—

$$\text{For ether } \frac{T-T'}{Tp}\times M = K = 0{\cdot}71.$$

Where K = constant, T and T′ the vapour pressures of the solvent and the solution respectively, p the percentage of solid, and M its molecular weight. Further, if M′ be the molecular weight of the solvent, then $\frac{K}{M'} = 0{\cdot}0105$ for all solvents.

This method may therefore be employed for the determination of the molecular weight of non-volatile substances, and offers in certain cases advantages over the method based on the depression of the freezing-point.

5. *Capillarity of solutions.*

79. Rother, 1884, W. 21, 576.
80. Volkmann, 1882, W. 17, 353.
81. Quincke, 1877, P. 160, 337, 560.

6. *Viscosity of solutions.* (*Internal friction.*)

82. Slotte, 1881, W. 14, 13; 1883, 20, 257.
83. Grotrian, 1879, W. 8, 529.
84. Sprung, 1876, P. 159, 1.
85. Poiseuille, A. Ch. [3] 21.
86. Hübener, 1873, P. 150, 248.
87. Wijkander, 1879, W. B. 3, 8.
88. Stephan, 1882, W. 17, 673.
89. Wagner, 1883, W. 18, 259.
90. Traube, 1886, B. 19, 871.
91. Noack, 1886, W. 27, 289; 28, 666.
92. Arrhenius, 1887, W. 1, 285.

7. *Diffusion of solutions.* (*Osmosis.*)

93. Long, 1880, W. 9, 613.
94. Fick, 1855, P. 94, 59.
95. Schmidt, 1857, P. 102, 122.
96. Graham, 1851, A. 77, 56, 129; 80, 197.
97. Weber, 1879, W. 7, 469, 536.
98. Stephan, 1879, Vienna Berichte, 79.

In 1855 Fick (94) put forward the tentative law, that the amount of salt which diffuses across a given area is proportional to the difference of concentration of two layers of solution infinitely near one another, *i.e.* is proportional to the gradient of concentration. The researches of Weber (97) completely confirmed this statement of Fick. Graham (96) made numerous experiments on this subject, and these were repeated and extended by Long (93), with the result of fairly confirming the results of the former experimenter (102).

When the diffusion takes place through a membrane (osmosis) the experimental difficulties are to a great extent overcome. An immense amount of experimental work has been done in this direction, but the most important is of comparatively recent date.

99. Pfeffer, W. Beibl. 2, 182.
100. Tammann, 1888, W. 34, 299.
101. Van't Hoff (66).
102. Ostwald, 1885, Stöchiometrie, 509.
103. De Vries, 1873, W. B. 3, 7; 1883, C. R. 97, 1083; W. B. 8, 282.
104. Donders and Hamburger, Zeits. für phys. Chem. 6, 319, 1890.
105. Adie, 1891, C. J. 60, 344.

If a porous cell be saturated with copper sulphate, carefully washed out, and then filled with a solution of ferrocyanide of potassium, it becomes coated inside with a continuous sheet of copper ferrocyanide, through which water, but not salt, can pass. In 1877 Pfeffer (99) found that if the temperature is constant the pressure produced by the passage of water through such a permeable membrane into a sugar solution placed in the cell is proportional to the strength of the solution of sugar. The pressures thus produced are very great indeed, *e.g.* 1 p.c. sugar gives 500 mm. of mercury, while 1 p.c. potassium nitrate gives 2,000 mm.

The proportionality thus found to exist between pressure and concentration is the same as that for gases, which is known as Boyle's Law. For if in a gas at any given pressure we double the number of molecules present, we double the pressure; so in a solution, if the number of active molecules (*i.e.* dissolved solid molecules) be doubled, the pressure (osmotic) is also doubled.

It has also been found that the effect of temperature on osmotic pressure is the same as on that of gases. That is, that the pressure (osmotic or gaseous) is directly proportional to the absolute temperature, or if the osmotic pressure at 0°C. $=p^\circ$, then at t°C. it will be $p^\circ(1+{\cdot}00367t)$—van't Hoff (102).

The gas equation $pv=RT$, where p = pressure, v = volume, T = absolute temperature, and R = a constant = 84·700 therefore holds good for solutions when p = osmotic pressure, and it follows that the osmotic pressure of a solution has the same value as the pressure that the solid would exert if it were contained as a gas in the same volume as that occupied by the solution.

It is also highly probable that the other gaseous law, that of Avogadro, is also applicable to solution, but the experiments which bear directly on this point are as yet but few in number.

Just as in vapours the pressure in some cases is much greater than the normal, reaching double the amount in cases such as ammonium chloride, owing to partial or complete dissociation, so in solutions it is found that many salts exert an abnormal osmotic pressure, that of potassium chloride, for instance, being nearly double the normal. It is, therefore, most probable that here, too, there is dissociation, and this explanation is supported by corresponding abnormalities in many of the other physical constants of the solutions of such salts.

8. *Optical properties of solutions.*

106. (45) [6] 463.
107. (45) [6] 479.
108. Russell, 1880, Pr. 31, 51; 32, 258.
109. Hartley, 1874, P.M. 391; 1876, 244.
    a. Refraction and dispersion (106).
    b. Rotatory power (109).
    c. Absorption spectra (108) (109).

9. *The thermo-chemistry of solutions. a. The heat of solution of salts in water.*

110. Thomsen, Thermochem. Untersuch. [2].
111. Berthelot, Mécanique Chimique.
112. Naumann, Thermochemie.

The most complete examination of this subject is due to Thomsen (110). The results at which he has arrived are summarised by him as follows:—

1. Those anhydrous salts which dissolve in water with evolution of heat form crystalline compounds with water, or are completely decomposed by it.

2. Those salts which do not form crystalline compounds with water, or are not decomposed by it, dissolve with absorption of heat.

3. The heat of solution of fully hydrated salts is negative.

4. The heat of hydration is positive.

5. The heat of solution is dependent on the atomic weights of the constituents of the salt as follows:—

(*a*) For similar compounds with the same halogen the heat of solution is greater the smaller the atomic weight of the metal; and

(*b*) For similar compounds of the same metal the heat of solution is sometimes greater the higher the atomic weight of the electro-negative constituent, as is the case with the salts of Mg, Ca, Sr, Ba, Na, sometimes less, as in the compounds of Cu, Cd, Au, Pb, Hg, Ag, Tl. The metals in this connection apparently range themselves in two groups, the light and heavy metals.

Consult also Berthelot (111).

(*b*) *The specific heat of solutions.*

113. Marignac, 1871, A. Ch. [4] 22, 385; [5] 8-410.
114. Person, 1851, A. Ch. [3], 33.
115. Schüller, 1869, P. 136, 70.
116. Pfaundler, 1870, B. 3, 798.

Solutions in general possess a lower specific heat than that calculated from those of their constituents, but the difference is generally less the stronger the solution.

Thomsen (57), Naumann (112).

10. *The electric conductivity of salt solutions.*

117. Kohlrausch, 1879, W. 6, 28 (summary).
118. Ostwald, 1889, Outlines, 266.
119. Arrhenius, 1884, Recherches sur la conductibilité, Stockholm.
120. Armstrong, 1886, Pr. 268.

The electrical conductivity of a solution increases rapidly with dilution, and usually reaches a maximum when the dilution is about 50,000 litres to the equivalent of salt in grms.

The conductivities of salts are additively composed of two quantities, one depending only on the metal, the other only on the acid radicle—Kohlrausch (117). For an account of the bearing of this special property of solutions on the general question of the nature of solution, reference must be made to Ostwald, van't Hoff, Armstrong, &c. The whole subject is too complex and extensive to be further dwelt on here.

11. *The supersaturation of salt solutions.*

121. Jeannel, 1876, C. R. 62, 37.
122. Tomlinson, 1868, Pr. 16, 403.
123. Bender, 1884, W. 22, 187.
124. Gernez, 1878, W. Beibl. 2, 241; C. R. 83, 217.
125. De Coppet, 1875, A. Ch. [5] 6, 275; C. R. 74, 328.
126. Löwel, 1857, A. Ch. [3] 49, 32.
127. Nicol, 1885, P. M. 454, 295; 1887, C. J. 51, 389.
128. Tilden, 1886, B. A. Report, Birmingham.
129. Roozeboom, 1889, Rec. des Trav. Chim. des Pays-Bas, 8, No. 1.

Supersaturation was first observed by Blagden. Whenever a solution retains more salt at a given temperature than can remain dissolved in contact with a crystal of the solid salt, the solution is supersaturated to that special form of the solid salt.

Jeannel (121) and Tomlinson (122) have maintained that only hydrated salts are capable of exhibiting the phenomena of supersaturation. Bender (123) and others, however, claim to have found that certain anhydrous salts also possess this property.

There is, however, but little doubt that only substances which exist in more than one crystalline form, whether with or without water of crystallisation, can form supersaturated solutions (Nicol, 127). This view has been recently confirmed by the work of Rooseboom (129) on the solubility of the various hydrates of calcium chloride and their modifications.

Supersaturated solutions can be prepared in various ways: By dissolving the salt to saturation at a high temperature, and then cooling the solution out of contact with the air; or by dissolving the more soluble modification in water in closed vessels after both salt and water have been heated to 110°—de Coppet (125), Nicol (127). Compare also Tilden (128).

There has been much discussion as to the causes which bring about the crystallisation of a supersaturated solution; but there is no doubt that the one cause which never fails is contact with a crystal of the salt itself or of an isomorphous salt.

Many other points of interest with regard to solutions have of necessity been omitted in this brief summary of the subject. The whole question is so far from being understood, that even now it is a moot point whether salts exist as such in solution or are partly dissociated into their constituent radicles. It cannot, therefore, be wondered at that the more complex branches of the subject are as yet far from being reduced to order. W. W. J. N.

SOMBRERITE. A mixed calcium and aluminium phosphate occurring on Sombrero and other islands of the Antilles (*v.* MANURES ARTIFICIAL).

SORANJES, or **SURANJI**, *v.* AAL, vol. i. p. 1.

SORBINOSE, **SORBIN**, or **SORBOSE**, $C_6H_{12}O_6$. A glucose obtained by fermenting the juice of mountain-ash berries, and probably formed by reduction of *sorbitol* $C_6H_{14}O_6$. Sorbinose forms rhombic crystals of a sweet taste, readily soluble in water, but only sparingly dissolved by alcohol. Reduces Fehling's solution, and is but slightly acted on by yeast. Is lævorotatory, the specific rotatory power of 10 p.c. solution being −43·4°. Is converted by nitric acid into trihydroxyglutaric acid, and when warmed with phenylhydrazine acetate forms *phenyl sorbinose azone* $C_8H_{10}O_4(N_2H.C_6H_5)_2$, melting at 164°.

SOUDAN BROWN *v.* AZO- COLOURING MATTERS.

SPANISH GRASS *v.* ESPARTO and PAPER.

SPANISH OCHRE. *Burnt Roman Ochre* *v.* PIGMENTS.

SPARTEINE *v.* BROOM TOPS; also VEGETO-ALKALOIDS.

SPATHIC or **SPATHOSE IRON ORE** *v.* IRON.

SPEARMINT-OIL *v.* OILS, ESSENTIAL.

SPECIFIC GRAVITY or **RELATIVE DENSITY.** The terms 'specific gravity' and 'density' are employed to indicate the relative masses of different kinds of matter which occupy equal spaces.

The term 'density' appears to be more accurate than the term 'specific gravity.' The latter involves the consideration of the action of the earth's attraction on the substances in question, but this attraction is not uniform over the whole of the earth's surface. It is true that no practical difficulty arises from this fact, for the specific gravity or density of a substance is determined by means of the balance, and a pound of water will equipoise a pound of platinum wherever the weighings are made. If, however, a spring balance were used, it would be found that the pound of platinum would be less attracted by the earth at the equator than at other parts of the earth's surface. If again we conceive this pound of platinum in space unattracted by any other matter (if such a spot exists) it could have no gravity, although the mass would remain unaltered; but the pound of platinum, whether at the equator or at the poles, or anywhere in space (provided its temperature were kept the same) would possess the same density, the same mass occupying the same volume. The term 'density' is almost universally employed with reference to vapours; 'vapour density' is a well-recognised expression, but we rarely hear of the specific gravity of a vapour. Again the point of maximum density of water is always spoken of; who ever heard of its point of maximum specific gravity? The term 'density' has been restricted so as to indicate the quantity of matter in unit volume, as pounds per cubic foot, ounces per cubic inch, or grms. per cubic centimètre, without actual reference to any standard; the ratios between these numbers and those of any standard body at a standard temperature and pressure will obviously be identical whatever units of mass and volume are employed.

The densities of solids and liquids are almost invariably compared with the density of water at 4°C. (or 39·2°F.), at which its density is higher than at any other temperature, the density of water under these conditions being taken as unity. The densities of gases and vapours are sometimes referred to that of hydrogen as unity, sometimes to that of atmospheric air; in the actual determination of the density, however, the comparison is almost always made with atmospheric air.

Densities of liquids.

The determination of the density of a liquid is perhaps a more simple operation than that of the density of solids and gases, so it may well be considered first.

One process is by finding the mass of liquid which exactly fills a vessel of known volume. A thin glass flask with a flat bottom, capable of holding about 50 c.c. or 25 c.c., is provided with an accurately-fitting stopper, through which a fine hole is drilled. The flask is first carefully weighed and then filled with the liquid, the temperature being noted. The stopper is then placed in the neck, the excess of liquid escapes through the perforation in the stopper, and is wiped off from the glass and the flask is again weighed. The flask is now emptied, cleaned, filled with distilled water, and again weighed. If the temperature of the water is the same as that of the liquid at the moment of putting in the stopper, then the weight of the liquid divided by the weight of the water gives the relative density of the liquid to that of water at the particular temperature. When great accuracy is required, a correction must be made for the quantity of air displaced by the liquid, and also by the weights. At the first weighing the flask was full of air, and therefore had a greater weight than it would have had if vacuous. When the liquid is poured into the flask this volume of air is displaced, and consequently the flask full of liquid weighs lighter by the amount of air displaced. On the other hand, the weights employed displace a quantity of air, and are thus a little lighter than they would be if used in vacuo, It is a laborious process to calculate the correction to be applied to each weighing, and tables have been constructed which enable the operator to find the correction at once when the density of the body weighed is approximately known. (Such a table will be found in 'Physikalisch-chemische Tabellen,' by Landolt and Börnstein.)

The specific-gravity bottle above described is not very convenient, for if the temperature of the balance case is above that of the liquid when the flask was filled, some of the liquid will escape by expansion and will be lost, and may injure the balance pan. It would be impossible to weigh the quantity of liquid which had been introduced into the bottle at the temperature of 4°, unless the temperature of the balance case were also at 4° or below, which would not frequently happen. To avoid this inconvenience there is ground into the neck of the flask a tube which is contracted in its middle to a capillary bore, and is provided at the top with a small reservoir closed by a stopper. To use this modification, the flask is filled and the tube inserted. This forces a small quantity of the liquid through the capillary tube into the reservoir above. The flask is now placed into a bath of known temperature, or even into water at 4°, and there left until its temperature is constant. If the liquid contracts so as to empty the reservoir above the capillary tube, a small additional quantity is introduced. When no change of volume is perceptible, a thin piece of filter paper or a fine glass tube is introduced into the reservoir so as to reduce the level of

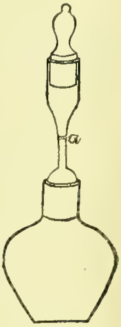


FIG. 1.

the liquid to a mark *a*, which is made on the outside of the capillary tube. The stopper may then be introduced into the reservoir, the flask removed from the bath and its outside dried, and it may now be left until it has reached the temperature of the balance case, where it can be weighed. In yet another form the specific gravity bottle consists of a flask with a long narrow neck, but not capillary. The neck is wide enough to admit of the introduction of a narrow thermometer, so that the temperature of the liquid may be determined in the bottle itself. The neck is provided with a mark to which it is to be filled, and is closed with a stopper.

Tribe (C. N. 1873, xxviii. 211–212) suggests the graduation of the tube by divisions half a millimetre apart. The contents of these divisions must first be accurately determined. The liquid may be introduced into the flask without any trouble being taken to bring the level of the liquid to any exact point. The flask is then cooled to the required temperature, and the volume determined by the graduation. If the flask, first empty and then full of water to the mark at 4°, be weighed, and the correction made for weighings in vacuo, the volume of the flask in cubic centimetres will be at once obtained, and this will avoid the necessity of weighing it filled with water in subsequent determinations if proper corrections are employed. When great accuracy is required, allowance must be made for the alteration of the volume of the flask by change of temperature.

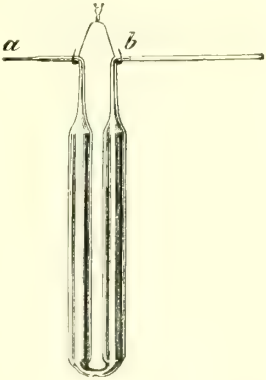


Fig. 2.

Instead of using a flask, Mathiessen and Hockin (the 'Laboratory,' 1867, p. 191) suggested the use of a capillary tube with a small bulb blown on it, with a capacity of only about three quarters of a cubic centimetre. The bulb is filled by dipping one end of the capillary tube in liquid and aspirating through the other end. The liquid is brought to the correct volume by touching one end of the capillary with the finger, when some of the liquid is removed and the level sinks to a mark on the other capillary, the space thus occupied being taken as the measured volume in all cases. They give some determinations of the density of ether by this apparatus, which agree well with a determination made in a bottle holding about 60 c.c.

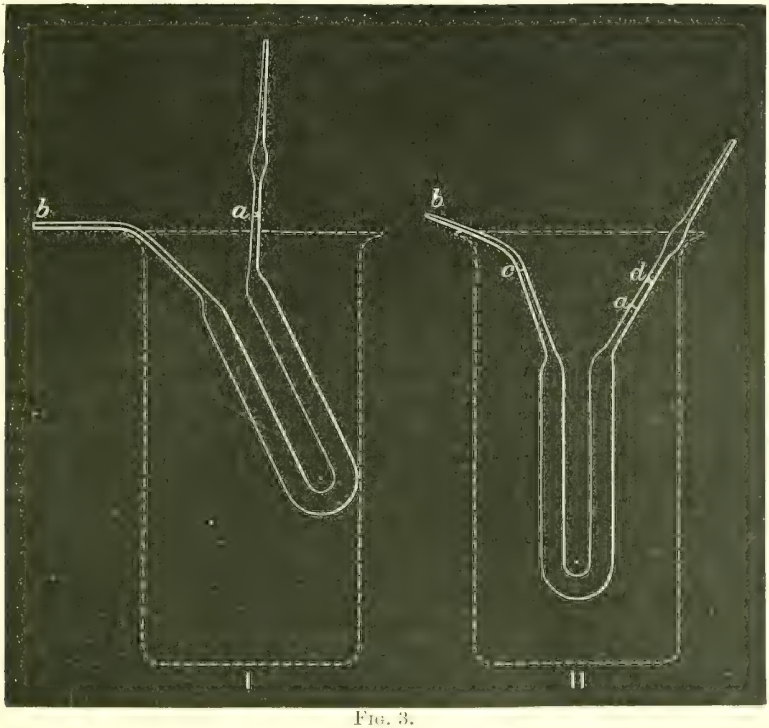


Fig. 3.

Sprengel (C. J. 1873, 577) describes the use of a U-shaped tube terminating in two capillary tubes bent in opposite directions. The liquid is aspirated into the tube, which is then sunk in a beaker of water, the capillary tubes resting on the edge of the beaker, and when the temperature of the contained liquid is constant, shown by the cessation of movement of the liquid in the capillary tube, some of the liquid is removed from one capillary, which terminates in a fine point *a*, by means of a piece of filter paper, until the liquid in the other capillary reaches a mark *b* near the bend. Some very accurate results are given in the paper which were obtained from a tube of about 18 c.c. capacity.

The liquid in the tube is in contact with the air at the extreme point *a*, and if very volatile there is some loss. In addition to this, Perkin (C. J. 1884, 45, 443) found that the moisture in the air was condensed in the form of snow at this point, and acted like a sponge, withdrawing more liquid from the tube. To avoid this inconvenience he slightly modified the form of the apparatus by bending the narrow tubes at obtuse angles instead of right angles, and making a small bulb on one of the tubes. A mark *a* is made below the small bulb on one of the limbs, the other limb terminating in a fine opening. After the liquid has been introduced into the tube, the latter is immersed in a beaker of water until the temperature of the liquid is constant. The tube is then inclined into the position I, and a piece of filter paper placed in contact with the point *b* until the liquid in the other limb falls to the mark *a*; the filter paper is withdrawn, and the tube restored to the vertical position. The liquid recedes from the end *b* of the tube and rises in the other limb, and if the temperature increases before weighing, the small bulb offers sufficient space to contain the liquid and thus prevent overflowing. The capacity of the tube was 5 or 10 c.c.

In the arts, the densities of liquids are most usually determined by means of the hydrometer. This instrument depends on the fact that when a solid floats on a liquid, the weight of the liquid displaced is equal to the weight of the floating body. The general form of the hydrometer is a spherical or cylindrical bulb, with a narrow stem, and the bulb is weighted at the bottom so that the instrument floats vertically in the liquid. The hydrometer is usually made of glass, but when it is employed for the determination of the strength of alcoholic liquids it is frequently constructed of brass.

When the hydrometer is placed in a liquid, it sinks until it has displaced a quantity of liquid equal to the weight of the instrument; it then floats in a position of equilibrium. If placed in a liquid of higher density it will not sink so deep, for the volume of this latter liquid possessing the same weight as the hydrometer will be smaller than in the first case. Again, when placed in a liquid of less density, it will sink deeper, for a larger volume has to be displaced before the weight of the hydrometer is supported. The density of the liquid is found by readings of the graduations marked on the stem. The most convenient graduation of the stem is one that gives the density at once, but there are other methods employed in graduating the stems.

When the stem is divided to show densities, the divisions are not of equal length, the differences of length being proportional to the differences of the reciprocals of the densities, and to render unnecessary such a division, hydrometers are frequently graduated with divisions of equal length, tables being employed to convert the readings into densities.

If the instrument is to be used for a long range of densities, the stem must be long and the bulb small, but an instrument of this kind does not give accurate results. It is much more convenient to have a set of hydrometers. Thus a set of four, the first for liquids between ·7 and 1·0, the second from 1·0 to 1·3, the third from 1·3 to 1·6, and the fourth from 1·6 to 1·9. A set of twelve is even still more convenient, each having a range of ·1; such a set may be graduated to the third place of decimals, and as each instrument is only about six inches in length, a comparatively small quantity of liquid is sufficient for the determination.

One form of graduation of hydrometer that is frequently used on the Continent and in America is Baumé's. The graduations on the stem are all equal, and the scale is fixed according to Baumé's directions in the following manner. For liquids denser than water, fifteen parts of pure sodic chloride are dissolved in 85 parts of water, at a temperature of 10°Réaumur (12·5°C. or 54·5°F.). The zero of the instrument is the point to which the hydrometer sinks in distilled water, and the point to which it sinks in the 15 p.c. solution of salt is marked 15. The distance between the zero and this point is divided into 15 equal parts, and the whole stem graduated with similar divisions. For liquids lighter than water the zero of the hydrometer is fixed by a 10 p.c. solution of sodic chloride, distilled water giving the division 10. This instrument is, of course, graduated in the opposite direction, the zero being at the bottom of the scale. Notwithstanding the very definite directions given for graduating the scale, it appears that the instrument-makers have departed from it, and in 1881 Professor C. F. Chandler read a paper before the National Academy of Sciences at Philadelphia, in which he states he has found twenty-three different scales for the hydrometer for liquids heavier than water, no one of which can be said to be correct; and for liquids lighter than water he has found eleven different scales. Baumé's idea was that each degree of his scale would give the percentage of salt present in a solution, and on this assumption many instrument-makers seem to have employed the 10 p.c. solution for graduating both instruments. Others have used oil of vitriol as the standard for 66°, but as oil of vitriol is by no means constant in its density errors have been introduced.

Professor Chandler gives the tables on next page for the values of the degrees of Baumé's hydrometers from experiments conducted in exact accordance with Baumé's original directions. The density for the 15 p.c. salt solution used for the calculation of the first table is the mean of thirteen determinations by different observers.

Another form of hydrometer is Sykes's, which is ordered by Act of Parliament to be used for the determination of the strength of alcoholic liquors. The instrument is made of brass, and has a flat stem divided into 10 parts, each of which is again divided into two. On the stem connecting the hollow bulb with the knob at the bottom, which causes the instrument to float vertically, slotted circular weights can be placed so as to extend the range of the instrument. These weights have the proportions 10, 20, 30, up to 90. The hydrometer is adjusted so that it sinks to 0, when no weight is on the stem, in alcohol of a density of ·825 (the standard alcohol of the Excise) at 60°F. In liquids containing more water the hydrometer, of course, does not sink so deeply, and by noting the temperature of the liquid and the number on the weights used, and the figures on the stem at the surface of the liquid, the quantity of the proof spirit in the sample can be found by reference to tables (*v.* ALCOHOLOMETRY).

Table for liquids heavier than water.

Value of degrees Baumé calculated from 0° = 1, and 15° = 1·1118988. Temperature 10°R. = 12·5°C. = 54·5°F.

Baumé degs.	Specific gravity	Baumé degs.	Specific gravity	Baumé degs.	Specific gravity
0	1·00000	26	1·21129	52	1·53580
1	1·00675	27	1·22122	53	1·55179
2	1·01360	28	1·23131	54	1·56812
3	1·02054	29	1·24156	55	1·58479
4	1·02757	30	1·25199	56	1·60182
5	1·03471	31	1·26260	57	1·61923
6	1·04194	32	1·27338	58	1·63701
7	1·04927	33	1·28436	59	1·65519
8	1·05671	34	1·29552	60	1·67378
9	1·06426	35	1·30688	61	1·69279
10	1·07191	36	1·31844	62	1·71223
11	1·07968	37	1·33021	63	1·73213
12	1·08755	38	1·34218	64	1·75250
13	1·09555	39	1·35438	65	1·77335
14	1·10366	40	1·36680	66	1·79470
15	1·11189	41	1·37945	67	1·81657
16	1·12025	42	1·39234	68	1·83899
17	1·12873	43	1·40547	69	1·86196
18	1·13735	44	1·41885	70	1·88551
19	1·14609	45	1·43248	71	1·90967
20	1·15497	46	1·44638	72	1·93446
21	1·16399	47	1·46056	73	1·95989
22	1·17316	48	1·47501	74	1·98601
23	1·18246	49	1·48975	75	2·01283
24	1·19192	50	1·50479	76	2·04038
25	1·20153	51	1·52014		

Table for liquids lighter than water.

Value of degrees Baumé calculated from 0° = 1·0737665 at 10° = 1. (The density of the 10 p.c. salt solution is the mean of nine observations.) Temperature 10°R. = 12·5°C. = 54·5°F.

Baumé degs.	Specific gravity	Baumé degs.	Specific gravity	Baumé degs.	Specific gravity
10	1·00000	35	·85342	60	·74432
15	·96679	40	·82912	65	·72577
20	·93571	45	·80616	70	·70811
25	·90657	50	·78443	75	·69130
30	·87919	55	·76385		

Twaddell's hydrometer, which is often used in England for liquids of greater density than water, is so divided that the numbers indicated on the stem, multiplied by 5 and added to 1,000, give the density of the liquid referred to water as 1000. Thus

20° Twaddell = a density of 1,100 or 1·100
100° „ = „ „ 1,500 or 1·500

Nicholson's hydrometer consists of a cylindrical metallic bulb connected at the bottom by a wire to a cup, and also an inverted cup pierced with holes. The top of the float is connected by a wire to a pan, on which weights may be placed. This wire has a single mark on it, which is brought to the surface of the liquid by weights placed on the upper scale pan. The instrument is so adjusted that when floating in distilled water at 62°F., 1,000 grains placed on the scale pan will bring the mark on the stem to the surface of the water. When placed in a denser liquid, more weights have to be added to the 1,000 grains in order to bring the mark to the level of the liquid, and as the same volume of liquid is displaced as in the case of the water, the weights at once give the density of the liquid referred to that of water at 62°. The cups below the float are used in the determination of the densities of solids, and will be referred to subsequently.

Another form of hydrometer depending on the same principle as Nicholson's consists of a cylindrical glass weight suspended from the arm of a balance, and is so counterpoised that the balance is in equilibrium when the plunger is sunk in distilled water. When placed in liquids of other densities the weights have to be altered to bring the balance to equilibrium, and the weights, which are generally used in the form of riders, are so arranged that the density of the liquid is read off directly. A thermometer may be placed within the glass plunger with its bulb projecting below, so that the temperature of the liquid can be simultaneously determined.

Another method of determining the densities of liquids depends on the fact that if columns of two liquids of different densities are made to support one another, the lengths of the columns will be inversely as the densities. Many different forms of apparatus depending on this principle have been described. Perhaps the most simple is that of Alexander (A. Ch. 1847, 70, 137), which consists of an inverted glass U tube with the limbs graduated upwards from 0 near the open ends; at the bend of the tube a small exhausting syringe is attached, or more simply a tubulure closed by a stopcock, or a piece of caoutchouc tube closed by a clamp may be used. One of the open ends of the tube is placed in water, and the other into the liquid of which the density is sought, and the air rarefied in the tube. The liquids rise in the tube, and after adjusting the levels outside the tubes to the zero marks, the lengths of the columns are read off. If the column of the liquid of unknown density is drawn up 100 mm. the reading of the level of the water in the other tube at once gives the density. Capillarity will affect the readings unless the tube is so wide that the lower curve of the meniscus is not raised above the level of the liquid outside. If the tubes are narrower, the heights of the columns drawn up by capillarity when the tubulure is freely open to the air must be subtracted from the column finally measured. Other forms of apparatus have been described by Tate (P. M. 1859 [4] 17, 254); by H. Schiff (A. 1862, 121, 82), and by L. Weber (Beiblätter, 1879, 3, 770).

For some purposes the density of a liquid has to be determined at its own boiling-point. This may be done by suspending a specific-gravity flask filled with the liquid in another vessel containing some of the same liquid, which is raised to the boiling-point. This heats the contents of the flask, and when the liquid ceases to expand the stopper is placed into the bottle, which is then removed from the vessel, allowed to cool, and weighed (C. Schall, B. 1884, 17, 2201). A better method of determining densities at high temperature is by the use of the dilatometer, which is a kind of thermometer with a wide graduated tube, the capacity of the tube and bulb being accurately known. The density of the liquid is first determined by the ordinary specific-gravity bottle, and then some of the liquid is introduced into the dilatometer, the temperature of which is gradually raised, and the increase of volume measured. When the co-efficient of expansion has been thus determined, the density at any temperature may be calculated. A complete account of the methods of using dilatometers, and all the precautions necessary in manipulating with them, will be found in a paper by Thorpe 'On the Relation between the Molecular Weights of Substances and their Specific Gravities in the Liquid State' (C. J. 1880, 37, 155).

Densities of solids.

In determining the density of a solid it is necessary to find its mass, and also the mass of an equal volume of water, or, what comes to the same thing, to find the volume of the solid from which the mass of the water can be calculated. In some few cases this may be done by measurement, as, for example, the measurement of a cubic foot of a body, like stone, which may be cut into a regular shape. It more generally happens, however, that the solid is irregular in form, or even in powder, when other methods must be adopted.

One of the simplest methods is to place some water or other liquid of known density in a graduated tube and measure it, and then introduce a weighed quantity of the solid, and observe the rise of level of the liquid in the tube. Or the tube may be weighed before and after the introduction of the solid, the increase of weight giving the quantity of the solid introduced. (H. Schiff, Ann. Chem. u. Pharm. 1858, 107, 59, and J. Osann, Ann. Phys. u. Chem. 1859, 106, 334). Gentilé (J. Pharm. 1867 [4] 5, 401), uses a small bottle with a bulb at the top of 1 c.c. capacity. The bulb is connected to the bottle by a narrow tube with a mark on it, and there is another mark on a similar tube above the bulb. The bottle is filled with liquid to the lower mark and weighed; the solid is introduced until the liquid reaches the upper mark, and the whole again weighed. This increase of weight is that of 1 c.c. of the solid.

A similar process that may be employed when the solid is in small fragments or in powder is to fill a specific-gravity bottle with water, and counterpoise it on a balance. Some of the solid is then placed on the pan of the balance and weighed; the solid is now placed into the specific-gravity bottle, and the level of the water adjusted. On again weighing, the quantity will be found to be less than the previous amount, the difference being due to the quantity of water expelled by the introduction of the solid, and which, of course, occupies the same volume as the solid. The relative density of the solid to water at the same temperature is at once found by dividing the weight of the solid by the weight of the quantity of water expelled. Some precautions are necessary in this method. Many solids, especially in the form of powder, entangle a quantity of air, which replaces some of the water in the bottle, or may even cause some of the solid to float in the liquid. This may often be removed by placing the specific-gravity bottle containing the water and the solid in an air-pump receiver and exhausting the air; the diminution of pressure causes the entangled air to expand and form large bubbles, which readily escape from the surface of the water. In the case of solids that are soluble in water this method is obviously inapplicable, and it is necessary to use another liquid of known density which does not act on the solid. Petroleum or alcohol may be used, care being taken to determine the density of the particular sample of liquid used.

When the body of which the density is to be determined is of such a shape that it can be suspended by a piece of fine platinum wire, the piece is first weighed and then attached by means of the fine platinum wire to the hook at the bottom of a small scale pan. A vessel of water is placed under the scale pan, and the solid immersed in it. When a solid is thus immersed in water it displaces its own volume of water, and there is at the same time an apparent loss of weight; this is due to the surrounding water producing a pressure on the solid which is exactly equal to the pressure on the volume of water which the solid has displaced, and which previously kept the water in the vessel in equilibrium. The apparent loss of weight is therefore the weight of the quantity of water displaced by the solid, that is to say of an equal volume of water, so that we obtain the necessary data for determining the relative density of the solid at the temperature of the water at the time of the observation, the mass of the solid divided by the loss of weight in water being the density.

If the body is less dense than water it is obvious that its density cannot be determined precisely in this manner, for the solid will float. To cause it to sink, it is attached to a piece of metal of known weight and density. On weighing the two bodies together in water part of the apparent loss of weight is due to the displacement of the water by the metal and part by the displacement by the light body. The loss caused by the sinker can be calculated from its known weight and density, and this deducted from the total apparent loss of weight gives the weight of the water displaced by the body of which the density is to be determined.

In practice it is, however, better to determine the amount of water displaced by the sinker than to calculate it. The substance may first be weighed, and then the sinker attached by thin platinum wire to the scale pan and weighed; then a vessel of water placed under the scale pan, and the sinker immersed in it. The apparent loss will give the quantity of water displaced by the sinker. The substance is now also attached to the wire and weighed, together with the sinker, in water, and the difference between the weight and the sum of the weights of the wire, sinker, and substance is the weight of the water displaced by the sinker and substance. As the weight of water displaced by the sinker has been determined, the difference between these two weights is the amount of water displaced by the substance alone, and the weight of the substance divided by this number gives the density.

The weight of water displaced by the light body may be obtained by the employment of three weighings, whereas the method just described requires four. It depends on the following facts: when a body floats on a liquid it displaces a weight of the liquid equal to its own weight; if the body is now totally immersed there is an upward pressure due to the additional quantity of the liquid displaced; this flotation pressure, determined by weights added to the weight of the body, gives the weight of the liquid displaced by the whole solid. In determining the density of such a body it is therefore necessary to know its weight, the apparent weight of the sinker when immersed, and the apparent loss of weight when the light body is attached to the sinker and weighed under water. The difference between the two last weighings, added to the weight of the body in air, gives the quantity of water displaced by the solid. Thus if P is the weight of the light body, P′ the weight of the sinker in water, and P″ the weight of sinker and the light body in water, the density $D = \frac{P}{P' - P'' + P}$.

Nicholson's hydrometer (as previously mentioned) may be used for the determination of the densities of solids. Weights are placed in the upper scale-pan until the instrument sinks to the mark. The weights are removed, and the substance is placed on the pan, and weights added until the mark is again at the level of the liquid; the difference between the weights is the weight of the solid in air. The solid is then placed on the lower scale-pan if of a higher density than water, or underneath the inverted cup if of a lower density, and weights are placed on the upper scale-pan to restore equilibrium. From the numbers thus obtained the amount of water displaced by the solid can be calculated, and from this, together with the weight of the body in air, the density is determined.

There are some solids which must not be wetted by any liquid, in consequence of a possible change of composition, and in these cases the usual methods of determining densities are of course not available. Others which are porous retain air so persistently that errors may arise by the presence of quantities of air which cannot be removed. In such cases the instrument called the stereometer, invented by Captain H. Say of the French engineers (A. Ch. 1797, 23, 1–20), may be employed. This apparatus has undergone several modifications, and is now known as the volumenometer. Say's apparatus consists of a glass cup connected at the bottom to a long vertical tube, graduated both in millimetres and cubic centimetres. The edge of the cup is ground and may be closed by a greased glass plate. The tube is sunk in a vessel of mercury until the mercury reaches the zero at the top of the tube. The glass plate is then placed carefully on the cup, and the apparatus raised by means of a pulley which is used so as to prevent rise of temperature by touching the tube with the hand. The mercury now sinks in the tube, but not to the level of the liquid outside; the difference between the levels is read on the scale of millimetres on the tube, and the increase of volume on the graduations of capacity. From these readings, together with that of the barometer, the original volume of the gas in the cup can be calculated. On closing the cup the contained air was at the atmospheric pressure H and its volume x. When the cup was raised the volume was increased to $x + a$, a being the volume read off on the graduated tube, whilst the pressure on the gas at the second measurement was $H - h$, h being the difference of level between the mercury inside and outside the tube.

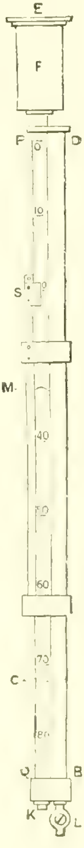


FIG. 4.

As by Boyle's law the volume of a gas multiplied by its pressure is a constant, $xH = (x + a)(H - h)$; hence $x = \frac{a(H - h)}{h}$. A numerical example will at once make this calculation clear. Suppose the volume in the cup to be taken as 1, the barometer standing at 760 mm.; if the cup is now raised until the volume is doubled, the pressure will be reduced to one-half. so the mercury will stand in the tube at 380 mm. above that outside. The increase of volume is therefore 1; then

$$x = \frac{1\,(760 - 380)}{380} = \frac{1 \times 380}{380} = 1.$$

The instrument is now sunk to the original level, the plate removed, and the body of which the density is to be determined is placed into the cup, the plate replaced, and the apparatus again raised. As the volume of air in the vessel is less than before there will be a smaller increase of volume for the same diminution of pressure, a second calculation will give the volume of air in the second case, and the difference between these two volumes is the volume of the solid introduced. From the volume and the mass, obtained by weighing, the density can be calculated. This apparatus was used for the determination of the density of gunpowder.

An instrument on this principle was constructed by W. H. Miller (P. M. 1834, 5, 203–204), and used by him to determine the density of the standard pound weights, which he was not allowed to weigh in water (Tr. 1856, 146, 799). It consists of a cylindrical iron vessel, to which a vertical glass tube of known contents is cemented. The lower end of the glass tube is attached to a hollow steel socket, to which a second tube, parallel to the first, is connected. The steel piece is also provided with a stopcock at the bottom, for the purpose of running out the mercury. A cup to hold the body of which the density is to be determined is first placed into the iron receiver, and mercury is poured into the open tube until it stands at the zero of the graduations of the tube attached to the iron cylinder. The cylinder is next covered with a greased glass plate, and the mercury allowed to flow from the stopcock until the pressure of the gas within the apparatus is reduced to about half an atmosphere. The difference between the levels of the mercury in the two tubes is then accurately measured, as well as the height of the barometer. The increase of the volume of the air is found from the previous calibration of the tube, which is done by allowing mercury to flow out from the tube and weighing the quantities which occupy spaces in the tubes between the graduations. From the increase of volume and the diminished pressure the volume of the original gas in the tube is calculated. The mercury is then restored to its original level in the open tube, the glass plate removed, and the standard weight introduced. The mercury is again run out, the measurements made as before, and the volume of the solid calculated, and from this, together with its weight, the density is found.

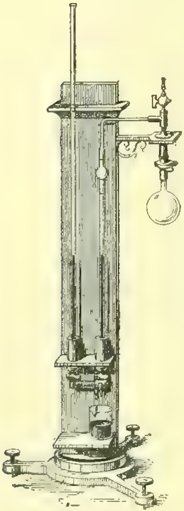


Fig. 5.

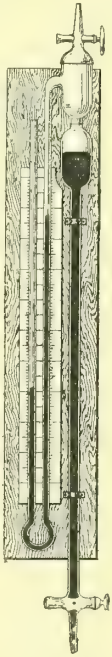


Fig. 6.

In 1845 Regnault published a note on a volumenometer (A. Ch. [3] 14, 207). This instrument (fig. 5) consisted of a globe of about 300 c.c. capacity, that could be united by means of metal flanges to a narrow tube connected to a manometer, and having a short branch tube provided with a stopcock, by opening which the pressure within the apparatus may be made the same as that of the atmosphere. The manometer was made of two parallel glass tubes, of which the one connected to the narrow tube had a bulb of about 60 c.c. capacity blown at its upper part. The globe was connected to the manometer, the stopcock communicating with the air opened, and mercury poured into the open tube until it filled the two tubes and the bulb at the top of the closed one, and rose to a mark on the latter tube. The stopcock was next closed, and mercury run out from another stopcock screwed to the steel piece connecting the two glass tubes until it reached a mark on the glass tube below the enlargement. The capacity of the space between the two marks being known, and the diminution of pressure being read by the differences of levels of the mercury in the two tubes, the original volume of air in the apparatus could be calculated. The globe was next disconnected and a weighed quantity of the substance to be experimented on introduced, and the process of measurement repeated. Of course this form of apparatus can be used only for powders or substances in small pieces. Grassi (J. Ph. 1847 [3] 11, 184) gives a number of determinations of densities made by this apparatus.

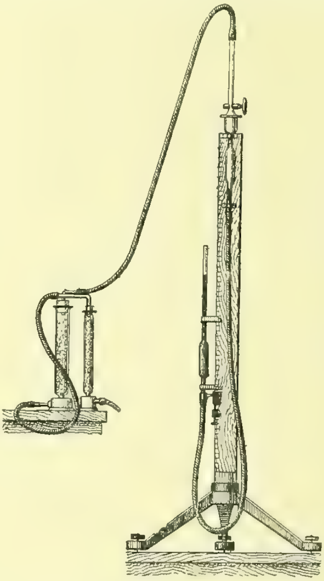


Fig. 7.

Another modification of the volumenometer was made by Rüdorff (A. 1879, N. F. 6, 288–293). This, which is made all of glass, consists of two vessels connected by a neck on which a mark is etched (fig. 6). The upper vessel, of a capacity of about 25 c.c., may be closed at the top by a ground cap furnished with a stopcock; the vessel is also provided with a U-shaped manometer tube. The lower vessel, of about 40 c.c. capacity, is joined to a long vertical tube, closed by a stopcock and having a mark near the top. The volume between the two marks is determined by running mercury out from the stopcock and weighing it. The operations are carried out in the same way as in the other forms of instrument. The upper stopcock being closed after the glass cap has been firmly fitted in its place, the mercury is then run out until its level reaches the lower mark on the tube, and the diminution of pressure is read by the manometer. The last form of the instrument appears to be that of Paalzow (fig. 7) (A. Ch. 1881, N. F. 13, 332–335). This, like the former apparatus, has a glass cup at the top attached to a glass tube, with a narrow neck at the top and bottom, on which lines are etched, the capacity between the two lines being accurately determined.

The lower neck is connected by a long caoutchouc tube to a similar glass tube or reservoir, with a narrower tube attached to each end, and of the same diameter as the necks of the measuring tube, to prevent any capillary depression of the mercury in the tubes. The reservoir is held by a clamp attached to the stand of the instrument, and which can be raised or lowered at will. It is first raised until the tube at the bottom of the reservoir is level with the upper neck of the measuring tube, and mercury is poured in until the caoutchouc tube and measuring tube are filled, care being taken that all air bubbles are removed from the sides of the tubes. The cup at the top of the instrument is closed by a perforated glass plate, to which a stopcock is fixed, and this may be connected to a drying apparatus, so that by lowering and raising the mercury reservoir several times the apparatus may be filled with dried air. To determine the density of a solid the mercury reservoir is raised until the mercury level in the measuring tube is exactly at the upper mark, the final adjustment being facilitated by using the micrometer screw attached to the clamp. The stopcock is closed, and the reservoir is lowered until the mercury is at the lower mark on the measuring tube. The difference of level is read off from graduations on the stand of the instrument, the barometer, of course, being read simultaneously. A repetition of the measurements with the substance in the cup gives the necessary data for calculating its volume.

The volumenometer obviously cannot be employed for the determination of the densities of solids which give off any gas or vapour under reduced pressure, such as efflorescent salts, for the increase of volume would be due not only to the expansion of the air in the apparatus, but also to the production of aqueous vapour. It answers very well for porous bodies like cotton wool, the entangled air from which at once expands on the pressure being diminished.

Another form of volumenometer was described by H. Kopp (A. 1842 [3] 6, 380), in which the air was compressed to a known extent and the increase of pressure measured. The apparatus is more complex than those above described, and might not be so easy of manipulation. It consists of a glass cylinder, into the bottom of which mercury is forced by means of a pump or plunger. The upper end of the cylinder is closed by a cover through which two glass tubes pass. One of these is a vertical tube open at both ends and extending nearly to the bottom of the cylinder. Two platinum wires with fine points are also attached to the inside of the cover, and extend to different depths inside the cylinder. The second tube through the cover communicates with the bottom of a cup, which can be closed by a glass plate held in position by a screw, the cup serving as the reservoir into which is placed the body whose density is to be determined. To use the apparatus, the glass plate is securely fitted to the cup, and mercury forced into the cylinder; air is expelled through the vertical tube until the mercury closes its lower end; the contained air now becomes compressed, and mercury rises in the tube. The admission of mercury is continued until its surface just touches the end of one of the platinum wires. The diminished volume is known from the capacity of the cylinder between the ends of the tube and of the wire, and the pressure is read by the difference of levels between the mercury in the cylinder and in the vertical tube. Another measurement is made with the cup containing the body, and from the two experiments the volume of the body is calculated.

Occasionally it is necessary to determine the densities of small fragments of crystals or minerals, and for this purpose Schaffgotsch (A. Ch. 1862, 116, 279) suggests the use of liquids in which the solids will just float. For substances lighter than water, dilute spirit may be employed, and for bodies more dense than water, nitric acid or solutions of common salt or of mercuric nitrate. The densities of the liquids may be afterwards determined, or a number of solutions of known densities may be kept in readiness. It is obvious that the method cannot be used if the solid is acted on or dissolved by the liquid; in this case other liquids may be used. Thus Sonstadt (C. N. 1874, 29, 127) used a mixture of ethylic iodide and carbon disulphide for determining the densities of potassic chloride, potassic sulphate, and alum, and for minerals a solution of mercuric iodide in a solution of potassic iodide may be obtained having a density of 3·085 at 12°. *V.* Goldschmidt (J. M. 1881; Beilageband, 1, 179), by a modification of Sonstadt's method, has obtained a solution of the double potassic mercuric iodide of the density 3·196. By the use of such a solution, diluted with varying quantities of water, the densities of very minute fragments of minerals may be approximately determined, thus enabling the mineralogist to recognise them very rapidly.

Dense liquids are now much used by petrologists for separating mixed minerals. From a quantity of crushed rock it is very tedious and difficult to pick out the various constituents by means of forceps; but, if the minerals have different densities, some will float in a dense liquid while others sink, and thus they may be readily separated. Thoulet (C. R. 1878, 86, 454) describes a mode of separating mixed mineral powders by placing the mixture in a solution of the double potassic mercuric iodide, when some of the more dense constituents sink to the bottom and are removed. On diluting the liquid with a known volume of water, the density of the solution is diminished and other constituents fall to the bottom. By repeating the process a fractional separation is affected.

D. Klein (C. R. 1881, 93, 318) suggested the use of the borotungstate of cadmium, a saturated solution of which has a density of 3·281. This salt fuses in its water of crystallisation at 75°, giving a liquid of a density of 3·6. This compound seems to be one of the most useful for the separation of mixed minerals.

A still denser liquid was obtained by C. Rohrbach (Ann. der Physik und Chemie, 2, 1883 [2] 20, 169) by combining mercuric and baric iodides. The solution has a density of 3·588, but the compound is unstable, for, on mixing with water, some mercuric iodide is precipitated, it also absorbs water from the air and its density is thus changed.

The use of methylene iodide CH_2I_2 was proposed by Brauns (J. M. 1886, 2, 72); this has a density of 3·33, and may be diluted with benzene if a less dense liquid is required. By dissolving iodine or iodoform in the methylene iodide, Retgers has obtained liquids with a density as high as 3·65.

For the identification of gems, Church employs standard solutions of the double potassic mercuric iodide of densities 3·17, 2·9, 2·67, and 2·63.

The use of fused solids has been suggested for the separation of mixed minerals. For this purpose the solid is fused in a test-tube, and the powder to be separated is thrown in and well stirred with the liquid, which is afterwards kept fused for a short time to allow the heavier particles to collect at the bottom and the lighter ones to float to the top. The substance is then allowed to cool, and the solid cylinder is removed from the test-tube, the upper and lower ends of the cylinder are cut off, and are acted on by suitable solvents when the separated minerals are left insoluble. The fused cadmic borotungstate has been already mentioned. R. Bréon (C. R. 1880, 90, 626) employs fused plumbic and zincic chlorides, and mixtures of the two. Plumbic chloride in the fused state has a density of 5, that of fused zincic chloride being 2·4, so that a considerable range is available. Unfortunately the plumbic chloride requires the high temperature of 400° to fuse it, and, as it is only sparingly soluble in water, it is not easily removed from the powders. Retgers mentions iodine as fusing at 113°, and giving a liquid with a density of 4; mercuric potassic iodide fuses at 160°, and the density of the liquid is 4·1; fused argentic nitrate has the same density, its fusing-point being 198°; and the mixture of argentic iodide and argentic nitrate fuses between 65° and 70°, and has a density of about 5. In order to facilitate the separation of powdered rocks by the use of heavy liquids, various forms of apparatus have been described by Church, van Werveke, Thoulet, Brögger, Harada, Oebbeke, Wülfing, Sollas, Smeeth, and Evans.

Density of gases.

The determination of the density of gases is a much more delicate operation than those for solids and liquids. In order to obtain a quantity of gas that can be weighed, it is necessary to employ a considerable volume. Again, gases are so much affected by changes of temperature and pressure that great precautions are necessary. Regnault employed flasks of a capacity of ten litres, and, when weighing one of the flasks containing a gas, another flask of the same kind of glass and of exactly equal external volume was suspended from the other pan of the balance. This second flask was hermetically sealed, and was used so that no correction for displacement of air by the experimental flask was necessary, and also that the film of moisture which is always deposited on glass vessels should not interfere with the weighings, for obviously the same quantity would be deposited on both flasks.

After the internal capacity of the experimental flask had been determined, it was connected to an air-pump and exhausted as completely as possible, and the pressure of the residual air determined by means of a manometer. The flask was then weighed, and it was assumed that its volume was the same as when it was full of gas of the ordinary atmospheric pressure. It was noticed by Agamennone (Rendiconti d. R. Accad. dei Lincei, 1885) that the volume must be smaller when the flask is vacuous and under the full pressure of the atmosphere. Lord Rayleigh has since shown independently (P. R. 1888, 43, 356) that the external pressure of the atmosphere very appreciably diminishes the external volume of the flask, so that the amount of air displaced by the vacuous flask is less than that displaced by the counterpoising flask. In his experiments the flask was about 1800 c.c. capacity, and the change of volume when exhausted was about ·43 c.c., which made a difference in weighing in air of ·00056 grms. When weighing hydrogen this amount of correction cannot be neglected. Regnault's method is necessary only for standard determinations of the densities of gases.

For chemical investigations the method of Bunsen is easily applicable. A flask with a narrow neck, and carefully-fitted stopper, has its neck graduated in millimetres, and the contents of the flask are determined by the method used in ordinary gas analysis, a table being constructed giving the capacity of the flask when filled to the divisions marked on its neck. Before use a small piece of potassic hydrate, or a little calcic chloride with a drop of water, is fused on to the interior of the flask. The flask is next filled with mercury, and inverted in a mercurial trough with glass sides (fig. 8). The gas is now passed into the flask from a delivery tube until the mercury is nearly all displaced. The apparatus is allowed to remain for some time in a room of constant temperature, and any water vapour the gas may contain is removed by the drying substance on the walls of the flask. During this time the stopper is held with its point just within the neck of the flask, being kept in this position either by a holder, which prevents its floating up by the pressure of the mercury, or by a thin platinum wire placed within the neck which keeps the stopper from closing it. After some time has elapsed the level of the mercury within the neck, and the level of the mercury in the trough, as measured on the neck, are read off by a telescope, the temperature of the gas, as indicated by a neighbouring thermometer and the barometer being read at the same time. From these data the volume of the gas at 0°, and at a pressure of 760 mm., is calculated. The stopper is now immediately fixed into the neck, by raising the holder or by removing the wire, and after it has been firmly fixed in its position the flask is removed from the trough and the mercury carefully wiped from the outside. The flask containing the gas and the small quantity of mercury is weighed. The stopper is now removed and a drying tube containing potassic hydrate is attached by a piece of india-rubber tube ; the whole is placed under the receiver of an air-pump, and the air pumped out and readmitted several times. By this means the gas is replaced by dry air, the potash tube is removed and the stopper replaced, the temperature of the flask and the barometer being simultaneously read. The flask, now containing a known volume of air at known temperature and pressure, is weighed, and from these data the weight of the air in the flask can be calculated. The difference between the weight found and the weight of the air calculated gives the weight of the flask and mercury, and this, subtracted from the weight obtained when the flask contained the gas, gives the weight of the gas, from which its density can be calculated.

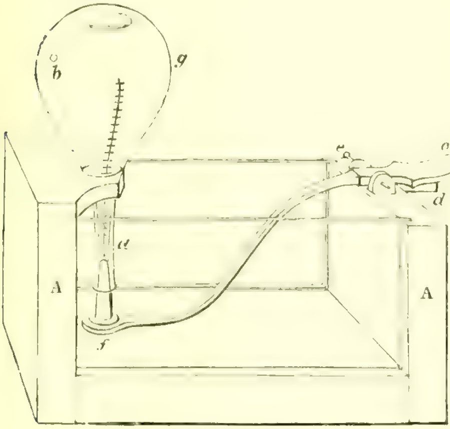


Fig. 8.

Another method for the determination of the densities of gases had been devised by Bunsen, and depends on the rate of effusion of the gases through a minute hole in a thin plate of platinum. The densities of two gases are proportional to the squares of the times of effusion, so the experiment consists in determining the time occupied by the passage of a certain volume of air through the aperture, and then determining the time required for the effusion of the same volume of the gas. The density in relation to air is obtained by dividing the square of the number of seconds obtained in the second case by the square of the number found in the first. This method is fully described in Bunsen's 'Gasometry,' and may be used with only a small volume of gas, and the results are sufficiently accurate for most practical purposes.

In the manufacture of coal gas it has been found convenient in some cases to be able to determine the density of the gas produced during the whole operation, and for this purpose an apparatus was devised by Bosscha and Ledoir (C. N. 1860, 1, 111) which gives a sufficiently close approximation for practical purposes. From the short arm of a balance with a bent beam, a sealed flask of about half-a-litre capacity is suspended. When placed in air the pointer on the long arm comes to rest at the zero of the graduated arc, over which the pointer moves. When placed in a gas of higher density the flask will be buoyed up and the pointer will fall; the reverse will occur if the gas is of less density than the air. Recently an arrangement has been contrived for making this apparatus self-recording.

Densities of vapours.

Two principal methods are employed in determining the densities of vapours. In one a known quantity of the body is volatilised and the volume of vapour measured, in the other a known volume is filled with the vapour and its weight determined.

Gay-Lussac's method is of the first kind. A graduated and calibrated tube is filled with mercury and inverted in an iron mercurial trough which can be heated below. A thin weighed bulb is filled as completely as possible with the liquid to be volatilised, sealed, and again weighed. The increase of weight is the quantity of liquid taken. This bulb is passed up into the graduated tube, which is then surrounded by a wider cylinder open at both ends, the cylinder being depressed below the surface of the mercury. Into the space between the cylinder and tube a liquid is placed to form a bath for heating the tube. This liquid may be water if the density of the vapour of a substance of low boiling-point is to be determined, or oil if a higher temperature than 100° is necessary. The mercurial trough is then heated, and the heat is conducted through the mercury to the liquid in the cylinder. The expansion of the liquid in the glass bulb bursts it, and as the temperature rises the liquid is transformed into vapour and depresses the mercury in the graduated tube. When the water in the cylinder boils, or the oil has reached a sufficiently high temperature, a thermometer in the bath is read and the level of the mercury in the graduated tube is noted, and also the atmospheric pressure at the time, by means of a barometer. It is next necessary to measure the difference of level between the mercury in the tube and that in the trough. This is done in one of two ways. In one a screw of known length working in a nut attached to the edge of the mercury trough is screwed down until its point just touches the surface of the mercury ; the difference of level between the top of the screw and the level of the mercury in the tube is now measured by means of a cathetometer, and the number thus obtained, added to the length of the screw, gives the difference of the level of mercury inside and outside the graduated vessel. In the other way a graduated steel rod, which can be clamped to a rod attached to the side of the mercury trough, is shifted so that its lower end touches the surface of the mercury. The graduated rod carries a slide with a projecting arm. This is moved until the lower edge of the arm is at the same level as the mercury in the tube; the reading of the graduated rod gives the desired difference of level.

From these data the density of the vapour can be calculated. It is necessary first to reduce the volume of the vapour to the normal pressure and the temperature of 0° on the assumption that the vapour could exist under these conditions without liquefaction. The volume V is obtained from the calibration table of the tube; the pressure under which the vapour existed is the height of the barometer, B, *minus* the difference of level, h, of the mercury inside and outside the tube, so that the whole correction becomes

$$V' = \frac{V \times (B - h)}{760 \times (1 + \cdot 003665t)},$$

t being the temperature of the bath at the moment of reading the volume of vapour and ·003665 the coefficient of the expansion of gases for 1° Centigrade starting from 0°. If great accuracy is required, the increase of capacity of the tube by rise of temperature must be corrected for, and also the alteration of the density of the mercury within the heated tube, and when high temperatures are employed the pressure of mercury vapour becomes considerable, and a correction must be made for it.

The weight of the corrected volume of vapour being known from the weighing of the thin glass bulb and the weight after filling, the density of the vapour may easily be calculated from the known weight of an equal volume of air or hydrogen.

If the substance is not quite pure it is obvious that the final result must be inaccurate, but if the whole of the substance is volatilised an approximation to the true density is obtained by this method.

Dumas' method of determining vapour densities is of the second kind, the weight of a known volume of the vapour being determined.

A light glass flask, of a capacity of from 100 to 350 c.c. (according to the density of the vapour to be determined), has its neck drawn out to a fine point and bent nearly at right angles. The flask has to be filled with dry air, which is done by connecting the point to a chloride of calcium tube and attaching the latter to an air-pump. The flask is several times exhausted, and filled with air which has passed through the drying tube. The flask full of air is now weighed, the temperature and the barometer being simultaneously read. The end of the tube is next dipped into the liquid, or the fused substance if the body of which the vapour density is to be determined is solid at the ordinary temperature, and by alternate heating and cooling some of the liquid is introduced into the flask. The flask is lowered into a bath of boiling water or of hot oil; the liquid boils, and its vapour expels the air. The introduction of the flask into the bath must be done with precaution, for a dangerous pressure might be produced in the flask if the evaporation were too rapid. When the temperature of the bath is well above the boiling-point of the liquid and vapour ceases to escape from the orifice, the point is sealed by a blowpipe flame, the temperature of the bath and the height of the barometer being observed at the same time. The flask is removed from the bath, cleaned, and weighed. The next process is to determine the capacity of the flask. For this purpose the point of the flask is broken under mercury, and the mercury is forced in by atmospheric pressure. If the mercury completely fills the flask it shows that no air was mixed with the vapour of the substance. The mercury is now poured out into a graduated vessel, and the quantity measured. This gives the volume of the vapour that the flask contained. If a bubble of air is observed above the mercury in the flask, its volume must be determined either by refilling the flask completely after measuring the mercury, or more conveniently by running mercury in from a burette until the flask is quite full of mercury with the condensed liquid above it; the volume of mercury thus introduced is equal to the volume of the residual air. The capacity of the flask is now determined by measuring the mercury as before described. The data are sufficient for the calculation of the vapour density; the weight of the flask is the weight first obtained *minus* the weight of the volume of air at the temperature and pressure at the time of weighing calculated from the volume of the flask found in the last operation. The weight of the vapour is the weight obtained in the second weighing *minus* the weight of the flask. The volume of the vapour at 0° and 760 mm. pressure is calculated from the volume of the flask and the temperature and pressure at the time of sealing, and the weight of an equal volume of air or of hydrogen is calculated from the known weights of a litre of these gases. A correction may be made for the increase of the capacity of the globe at the temperature at which it is sealed, but in most cases this correction is unnecessary. The coefficient of expansion of glass given by Regnault is as follows:

Between	For each deg. C.
0° and 100°	·0000276
0° „ 150°	·0000284
0° „ 200°	·0000291
0° „ 250°	·0000298
0° „ 300°	·0000306
0° „ 350°	·0000313

When Dumas' method is used the substance must be very pure, for if it is a mixture the portions with the lower boiling-point pass off first, and the density ultimately arrived at is vitiated by the presence of the substances of higher boiling-point present, whereas in Gay-Lussac's method the density is much less interfered with, provided the mixture is entirely volatilised.

Modifications of both these methods have been made. For very high temperatures Deville and Troost employed a porcelain flask heated in the vapour of mercury, sulphur, cadmium, or zinc. The porcelain globes were sealed by means of an oxyhydrogen blowpipe.

Hofmann (A. 1861, Suppl. 1, 9) modified Gay-Lussac's apparatus for the determination of the density of triethylphosphine oxide in the following manner. A U-shaped tube was made with one limb longer than the other; the shorter limb, which was wider than the other limb and the bend, was closed at the top and graduated into cubic centimetres. The narrow limb of the tube was provided with a narrow side-tube slightly inclined downwards. To use the apparatus, the side-tube was closed by a piece of caoutchouc tube and glass rod stopper, and the apparatus entirely filled with mercury, inverted, and the open end placed in the mercurial trough. A bulb containing a weighed quantity of the substance was then passed up the tube and round the bend into the closed limb. The tube was then placed in the erect position, and the stopper of the side-tube removed. The U-tube was next placed in a water or oil bath with the side-tube projecting over the edge. On heating the bath the substance volatilised, and the mercury expelled from the side-tube was collected in a bottle. When the mercury ceased to flow out it was weighed. From the known temperature of the bath and the weight of the mercury the volume of vapour in the closed limb can be calculated. On now removing the tube from the bath and measuring the vertical distance between the side-tube and the graduation on the closed limb representing the volume of the vapour which the tube contained when hot, the pressure under which the vapour existed is easily calculated, this pressure being obviously greater than that of the atmosphere at the time. From these data the density of the vapour may be calculated. A similar apparatus was described by Goldschmidt and Ciamician in 1877 (B. 10, 641), and by V. Meyer in 1876 (B. 9, 1216), who, however, filled the bulb with fusible alloy and heated in vapour of sulphur.

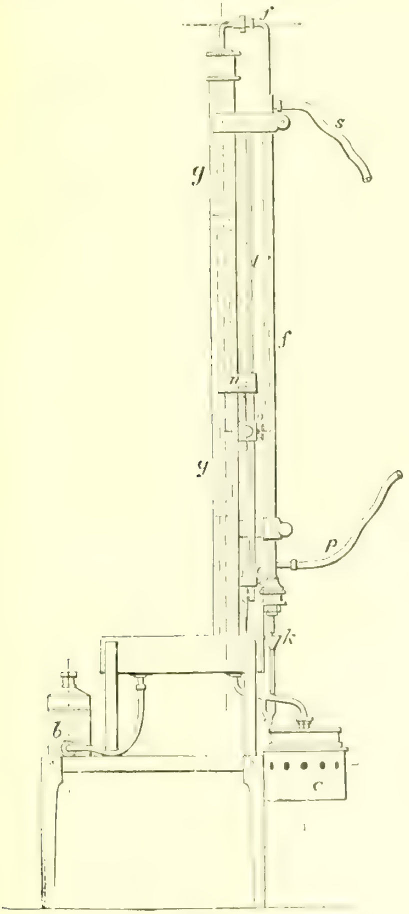


Fig. 9.

Hofmann employs a graduated tube of about a metre in length, standing in a mercurial trough, and heated by a jacket through which a current of the vapour of a liquid with high boiling-point is passed. Under these circumstances the vapour density is determined much below the atmospheric pressure, which enables the operation to to be carried out below the boiling-point of the body and also diminishes the chance of dissociation, which may sometimes occur. The volatile substance is placed in a small stoppered tube, which is introduced into the graduated tube.

Hofmann's apparatus has been further modified by Thorpe (C. J. 1880, 37, 147), fig. 9. Instead of the barometer-tube being graduated through its whole length, only one mark is etched on it near the closed end. The capacity of the closed end to the mark is first determined, and the rest of the tube is calibrated by pouring in known quantities of mercury as in calibrating a eudiometer, the levels of the mercury in the tube being read off by a graduated scale placed by its side. The mercury trough is provided with a shallow well in which the barometer-tube and the surrounding cylinder stand, and there is an opening at the bottom of the other portion of the trough by means of which the mercury may be drawn through a caoutchouc tube into a tubulated bottle. Through the bottom of the trough and into the well pass two nickel-plated copper tubes, one of which passes to the bottom and the other to the top of a copper boiler placed below the level of the trough, and containing the liquid the vapour of which is to heat the barometer. When an experiment is to be made the two copper tubes are connected by a short india-rubber tube (to prevent the access of mercury), and the bottle of mercury raised so as to fill the trough. The calibrated tube is next filled with mercury and inverted in the trough, and the weighed substance introduced. The tube is placed in the well, the mercury run out from

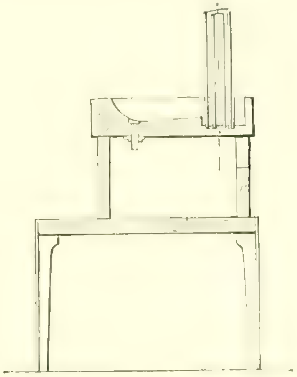


Fig. 10. Section of Mercury Trough.

the trough, and the india-rubber tube removed from the copper tubes. A wide cylinder is now placed round the barometer-tube so as to inclose the tubes connected with the boiler between the cylinder and the barometer, and to the top of the wide tube a cap is fitted connected to a vertical metal condenser, which also acts as the support of the glass tubes. The liquid in the boiler is now raised to ebullition, and the vapour which condenses in the cylinder returns to the boiler by the tube which passes to the bottom, and which is a little shorter than the other tube. Any vapour which passes through the cylinder is condensed by the vertical condenser and falls into a funnel attached to the return tube to the boiler. The mercury expelled from the barometer flows over the edge of the well, and runs into the bottle. In this form of apparatus the whole of the mercury in the barometer-tube is uniformly heated, which renders it possible to make an accurate correction for the pressure. When the vapour ceases to expand, the lower end of the steel scale is brought in contact with the mercury in the well, and the level of the mercury in the tube is measured by moving downwards by rack and pinion a piece of brass which partly surrounds the wide tube. This gives the height of the column in the barometer, and, by reference to the calibration table, the volume of the vapour in the tube.

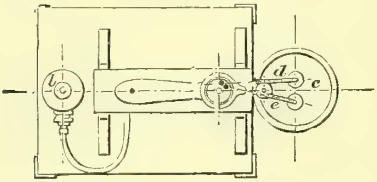


Fig. 11.—Plan of Mercury Trough.

Another process for the determination of vapour densities has been much used during the last few years. It was devised by V. and C. Meyer (B. 1878, 11, 2253), and depends on the measurement of the volume of air expelled from a closed vessel by the volatilisation of a known weight of the substance. The apparatus consists of a cylindrical bulb of about 100 c.c. capacity attached to the end of a long tube. Near the upper end of the latter a side-tube is attached which dips downwards into a water trough, and over the end of this delivery tube a graduated cylinder full of water may be placed, the top of the vertical tube being closed by a cork. At the bottom of the cylindrical bulb a quantity of asbestos is placed to prevent the fracture of the glass by the introduction of the vessel containing the body of which the vapour density is to be determined. The bulb and part of the long tube is heated in the vapour of a liquid of sufficiently high boiling-point, and when the temperature of the tube becomes constant (indicated by the cessation of escape of air through the water in the trough) the graduated tube is placed over the end of the delivery tube, the cork withdrawn from the long tube, and a small glass bulb, containing a weighed quantity of the substance, is placed within the open end of the tube. The capillary end of the bulb tube is broken off, and the bulb allowed to fall into the apparatus and the cork immediately replaced. The volatile body is rapidly transformed into vapour, and air is expelled and collected in the graduated cylinder. The evaporation takes place so rapidly that none of the vapour has time to diffuse into the cooler parts of the apparatus, and the air expelled, when reduced to the normal temperature and pressure, is equal to the corrected volume of the vapour produced from the weighed quantity of the substance. From the data thus obtained the vapour density is calculated.

Various devices have been invented for allowing the bulb to fall without opening the apparatus, so as to avoid a loss of air, and others which permit of the determination of vapour densities under reduced pressures.

By employing an apparatus constructed of more refractory substances than glass, the vapour densities of bodies may be determined up to temperatures as high 1700°, and much light has been thrown on the constitution of volatile compounds by these investigations.

H. McL.

SPECTRUM ANALYSIS, PRACTICAL APPLICATIONS OF.

I. Absorption Spectra.

Absorption spectra are best observed with an instrument which furnishes a brilliant spectrum with but small dispersion. A direct-vision instrument of small size, or one which is capable of furnishing angular measurements, and fitted with a compound prism of Grubb's construction, answers the purpose exceedingly well.

To secure greater accuracy in the description of spectra than is possible by means of curves not drawn to scale, and with only solar lines as references, it is desirable (1) that the strength of solutions be known, (2) that the thickness be recorded, (3) that the absorption bands be measured and reduced by an interpolation curve to wave-lengths or their reciprocals. The latter are termed *oscillation frequencies*, which indicate the number of vibrations made by each ray in a very small unit of time.

In the examination of ultra-violet spectra photography reduces much of the work to mechanical routine, with the advantage of a permanent record on the photographic plate which can be referred to at any time. Measurements are easily made by applying a straight ivory scale to the photograph, the scale being read by the aid of a magnifier. Measurements are stated either in tenth-metrets (ten-millionths of a millimetre) or in ninth-metrets (millionths of a millimetre).

The decimal subdivisions of a metre are conveniently termed *metrets* (Johnstone Stoney). The first metret is a decimetre, the second metret is a centimetre, the third is a millimetre, and so on. A *tenth-metret* $= (\frac{1}{10})^{10}$ metre = one ten-millionth of a millimetre.

For facility in reference, a scale of wave lengths applied to prominent lines in the solar spectrum is expressed in tenth-metrets extending from 8,000 to 2,000 (fig. 1).

(1) **The examination of ultramarine.** Various kinds of ultramarine show such different spectra that the manufacturer can at once ascertain the nature of any product he obtains. Wunder mixed the powder with a colourless oil in a glass

cell with parallel sides. The pigment may even be mixed with gum arabic or photographic varnish, and allowed to dry on a glass-plate (fig. 2). The *purest sunlight* should be used for these observations (H. W. Vogel, 'Praktische Spectralanalyse,' p. 237).

(2) **The examination of precious stones.** Garnets exhibit different absorption spectra according to their origin (fig. 3). Rubies exhibit a spectrum distinct from that of ruby-coloured glass. Emeralds yield a spectrum which cannot be communicated to glass by cupric oxide (H. W. Vogel, *l.c.*).

(3) **The recognition of various dyes and colouring matters.** The principle upon which the recognition of colouring matters depends is not alone their action on the spectrum, but upon a series of alterations in the spectrum brought about by treatment with various reagents. Stokes first showed the sensitiveness of these changes in optical properties, and Sorby first applied them to determining the nature of the colouring matters in wines, essences, liqueurs, inks, &c. It is first of all necessary to be able to recognise dyes by their spectra. The changes in their spectra should next be studied when various reagents are added (figs. 4, 5, and 6) (H. W. Vogel, *l.c.*).

(4) **The detection of foreign colouring matter in wine.** The true colouring matter of wine dialyses very slowly, if at all, through parchment paper. All other colouring matters, which, it is alleged, are made use of for fraudulent purposes, dialyse freely. There is one exception in the colour from alkanet root.

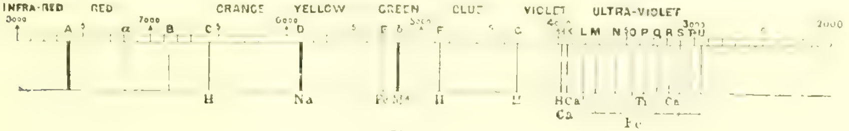


FIG. 1.

To test for coloured impurities in wine, prepare a jelly by dissolving 10 parts of gelatine and 10 of glycerine in distilled water. When by gentle warming the gelatine is properly dissolved, pour it into a photographic dish, or a paper mould, so that it forms a layer about $\frac{3}{4}$ inch in depth. When the jelly has set, cut it into squares, the sides of which measure $\frac{3}{4}$ inch, with a sharp wet knife. These cubes of jelly are placed in the wine to be tested. If, after a shorter or longer interval of immersion, such a cube is taken out, washed with a little water, and a central slice is cut out of it in a direction parallel to the sides, it will be found in the case of a pure wine that the colour has penetrated but a very little way into the cube ($\frac{1}{16}$ in. in the course of 24 to 48 hours), whereas many other colouring matters penetrate to the very centre of the cube.

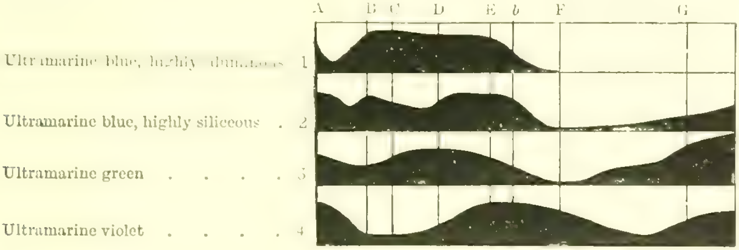


FIG. 2.

In the case of alkanet root, which does not penetrate the jelly, the characteristic spectrum exhibiting three distinct absorption bands will serve to distinguish it. Ammonia turns wine a greenish-brown, but alkanet becomes a beautiful blue, the absorption bands being reduced to two in number (fig. 7). Usually it suffices to show that the wine is artificially coloured, but when it is desirable to go farther, the colour of the slice of jelly, its absorption spectrum, or the action of ammonia upon it leads to its detection. It is a strong proof of the presence of a foreign colouring matter in a red wine if the colour shown by the slice differs from that of the wine. Indigo and logwood, for example, are thus readily detected.

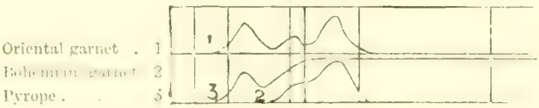


FIG. 3.

A foreign colouring matter having been proved to be present by means of the cubes of jelly, a larger quantity of wine is submitted to dialysis in a parchment paper dialyser. When a sufficient amount of colouring matter has dialysed, the liquid may be examined, either directly or after careful concentration, and the spectrum may now be observed without being complicated or obscured by the colouring matter of the grape.

Colouring matters which penetrate but slowly into the jelly:—

Colouring matter of pure wine.
" " alkanet root.

Colouring matters which rapidly penetrate the jelly:—

Althea officinalis
Althea rosea (hollyhock).
Beetroot
Bilberry
Brazil wood
Carnations (*Dianthus caryophyllus*)
Cherry, red, sour
Cherry, black
Clematis, purple
Cochineal
Cranberry
Currant, red
Currant, black
Elderberry
Indigo
Litmus
Logwood
Malvea sylvestris
Raspberries
Red cabbage
Red poppy
Rhatany root
Rosaniline
Saffron
Strawberry

In most cases if 10 p.c. of the colour is obtained by fictitious means, the wine will yield distinct results with these cubes (A. Dupré, C. J. 37, 572–575).

Rosaniline hydrochloride may be detected in wine by warming the liquid, and shaking with a piece of stearin, which becomes dyed. With natural wine it becomes discoloured only. When warmed with amylic alcohol, the stearin parts with its colour, which may then be recognised by the spectroscope. Sodium rosaniline-sulphonate dyes the stearin a bluish violet. In *neutral* solutions this reaction is not very sensitive (C. H. Wolff, C. C. [3] vol. 13, 670).

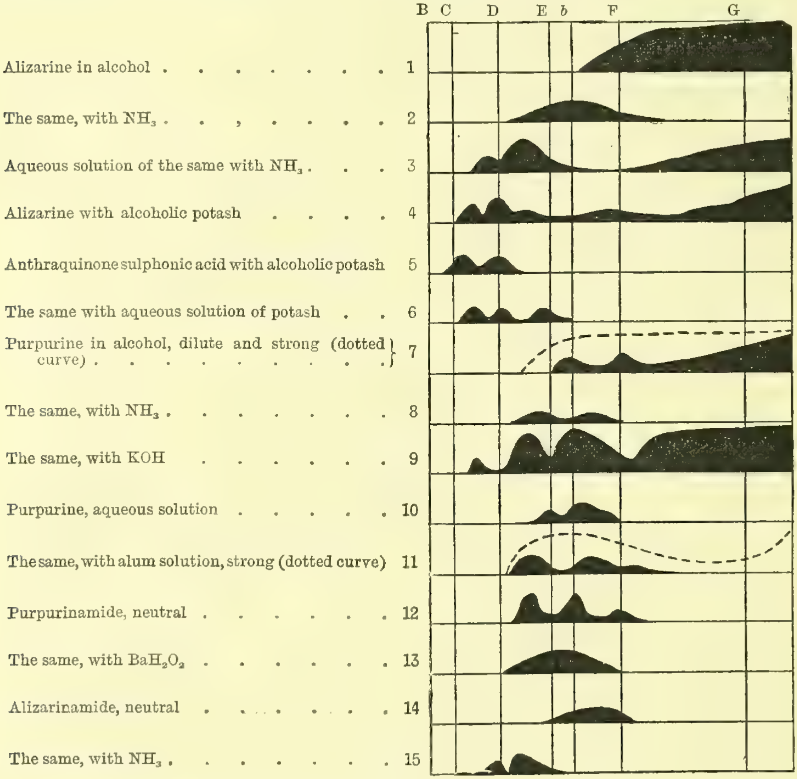


Fig. 4.

The detection of fuchsine (rosaniline hydrochloride) in syrup of raspberries cannot be made satisfactorily by dialysis. A few drops of nitric acid should be added to the syrup previous to shaking it with amylic alcohol to dissolve the fuchsine. Natural raspberry juice yields a colour to amylic alcohol, with an absorption spectrum resembling that of the dye (H. W. Vogel, B. 10, 1428–1432, 1877).

(5) **The detection of alum in wine and fruit juices.** Alum and alumina are used in the 'fining' of wine, but the presence of organic substances prevents the alumina being detected in the ordinary manner except with great difficulty. Lime must first be removed by treatment with ammonium carbonate, and a slight subsequent addition of ammonium oxalate. It is not advisable to precipitate the lime with ammonium oxalate alone, because the precipitate is too long in settling. Filtration is to be avoided, because traces of magnesia are apt to remain upon the filter. The excess of ammonia and ammonium carbonate are removed by acetic acid. It is best to add a very slight excess, and remove this with dilute ammonia.

In examining fruit juices, first of all remove the colouring matter by destroying it with a little perfectly-pure sodium hypochlorite and hydrochloric acid. To detect very small quantities of magnesia and alumina proceed as follows:—To 2 c.c. cautiously add ammonia, neutralise with acetic acid, so dilute that 1 drop neutralises 2 drops of the ammonia; add 1 drop of dilute solution of ammonia in excess (1 to 4 of water by volume). Then add 3 to 4 drops of alcoholic solution of perfectly-pure purpurine for each c.c. of solution to be tested. It may be purified by sublimation or by solution in ether. Characteristic absorption bands will then instantly appear (see fig. 4). Cautiously acidify with acetic acid, and the bands will instantly disappear if only magnesia is present. If alumina alone be present, the bands are unaltered. If both magnesia and alumina are present, the addition of acetic acid will only weaken the bands. In presence of much ammonium chloride it is recommended that a few more drops of purpurine solution be added in order to obtain a marked difference between the reactions due to magnesia and to alumina. Under such conditions $\frac{1}{10}$th of a milligram can be recognised.

Some wines contain iron, which metal interferes with the reaction; add a little tartaric acid, excess of ammonia, precipitate the iron with ammonium sulphide, and filter. Acidify the filtrate with the least possible quantity of hydrochloric acid, boil, and filter to remove sulphur. To this solution the test may be added as directed (H. W. Vogel, *l.c.*).

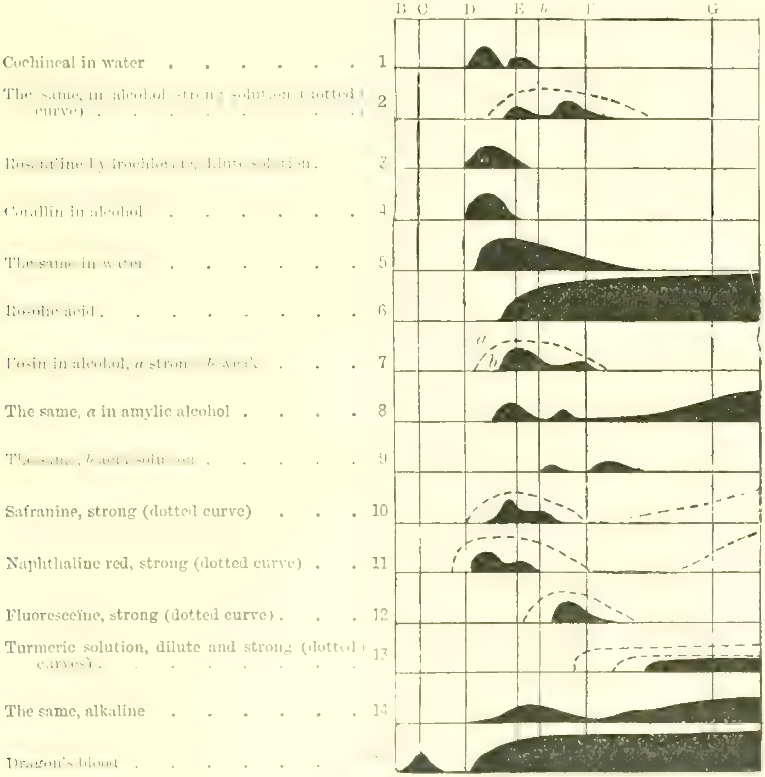
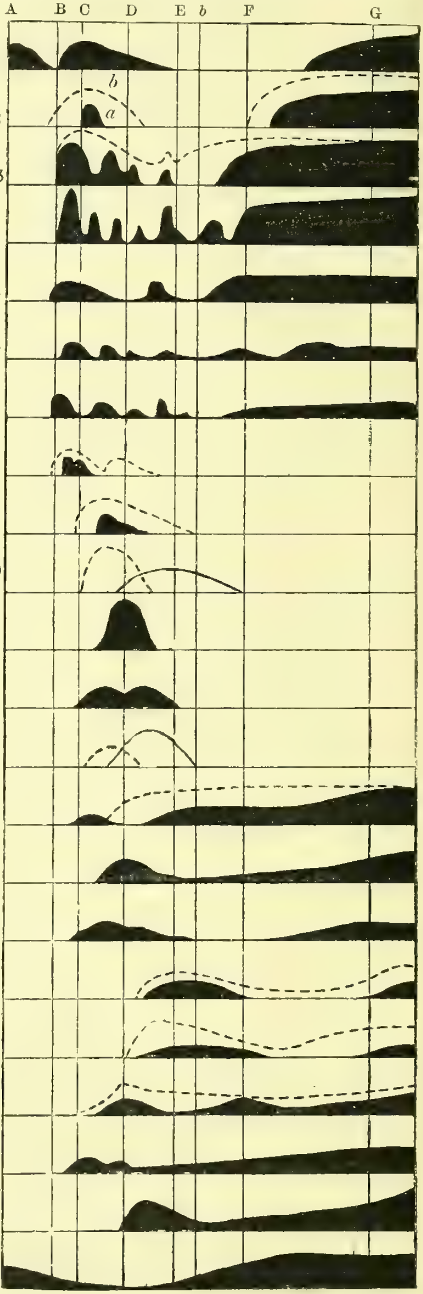


Fig. 5.

(6) **The detection of blighted wheat in flour.** Ordinary methods for detecting blighted corn in flour lack certainty, and fail to detect a small percentage. When flour made from blighted corn is extracted with alcohol, the fat and resin are removed, together with a brownish colouring matter. When a few drops of dilute hydrochloric or sulphuric acid are added to the violet-grey residue, the colour changes to a fine red. This red substance is easily soluble in cold alcohol, ether, amylic alcohol, benzene, and chloroform, and the character of its spectrum serves to identify it. Strong solutions, or thick layers of dilute solution, transmit the red rays only; on gradual dilution there appear, first the yellow, then the green, and finally the whole spectrum, exhibiting two bands of absorption, which remain visible even after extreme dilution, and which are highly characteristic. One lies near E, but the broader and stronger is situated between F and G. These bands appear with less intensity in the brown extract of flour. Though the red substance is soluble in water and weak spirit, it is removed therefrom by shaking with ether, amyl alcohol, chloroform, and benzene. All these solvents display the bands, but ether shows them most distinctly.

The process.—Boil 20 grms. of flour with alcohol for five minutes, the liquid being constantly stirred, and alcohol being replaced as loss occurs by evaporation. Allow to settle, and pour off the extract. Repeat until the alcohol ceases to be coloured. Add 20 drops of cold dilute sulphuric acid, and stir briskly; allow the liquid to stand, and decant through a filter. Examine by the spectroscope in thick or thin layers, according to depth of colour. About 10 c.c. are mixed with about 20 c.c. of water, and the turbid liquid is shaken with about 2 c.c. of amylic alcohol; other three portions are similarly treated with chloroform, benzene, and ether respectively. If all four solvents exhibit the absorption spectrum, the bands being slightly displaced owing to the different refraction



Iodine green	1
Methyl rosaniline picrate—*a* weak solution, *b* strong . .	2
Chlorophyll in alcohol, a fresh solution, very strong (dotted curve)	3
The same, an old solution	4
Chlorophyll in alcohol + trace of HCl, action commencing	5
The same, action complete	6
The same, + HCl in excess	7
The same, + KOH, strong solution (dotted curve) . .	8
Indigotine dilute, strong (dotted curve)	9
Aniline blue in alcohol (dotted curve), in water (plain curve)	10
Methyl violet	11
Syrup of violets	12
The same, acid (plain curve), alkaline (dotted curve) . .	13
Red wine + NH_3, pure (dotted curve)	14
Bilberry juice with NH_3	15
Tincture of mallow with NH_3	16
Bilberry juice (dotted curve). The same, with tartaric acid	17
Elderberry juice (dotted curve). The same, with tartaric acid	18
Privet berries (dotted curve). The same, with tartaric acid	19
Privet berries with NH_3	20
Raspberry juice	21
The same, with NH_3	22

Fig. 6.

equivalents of the solvents, the presence of blighted wheat is proved.

Measurement of the bands. With a large instrument the number of bands is ascertained to be three lying between E and G. The following are the mean rays absorbed :—

Band I.	II.	III.
5364	4975	4656.

These are similar to Bands IV., V., and VI. of an ethereal solution of chlorophyll (J. Petre, Z. 1879, 211–220; C. J. 36, 977–979).

(7) **The discrimination of anthracenes.** An examination of anthracene by the spectroscope has proved a valuable preliminary test and adjunct to known methods of examining crude or commercial anthracenes. Ordinary yellow chrysene which accompanies hydrocarbons of high melting-point, and occurs in commercial anthracene, is an indication of the presence of matters which are objectionable, and being prejudicial in the processes to which anthracene is submitted in the preparation of alizarine, it is desirable that their presence be determined. Chrysene exhibits superb absorption bands, broad and deep, two between the F and G lines, and one a little more refrangible than G. The substance is not chrysene itself but an impurity, a phenylen-naphthalenimide of a beautiful green colour $\left.\begin{matrix}C_6H_4\\C_{10}H_6\end{matrix}\right\}NH$ described by Graebe. Its fusing-point is as high as 330°C.

A few grains of the sample of anthracene to be tested are placed in a test-tube, a little benzene is added, and warmed so as to dissolve the contained anthracene. Finally, it is made up to 6 c.c. with more benzene, and passed through a paper filter to remove water. A pocket spectroscope is then applied to the tube, and the absorption bands are seen as dark lines, or as very narrow bands, the depth or intensity of which indicates the quantity of material present (B. Nickels, C. N. 41, 94, 1880).

(8) **Reactions of some alkaloids and glucosides.** *Digitaline* boiled with strong hydrochloric acid acquires a greenish yellow colour, and exhibits a large black band at the commencement of the blue rays near F. The remainder of the blue is visible, whilst the violet rays are absorbed from half way between F and G.

When the reaction is made with strong sulphuric acid, a reddish-brown solution is obtained, which shows two very distinct black bands. One occurs in the green at E, *b*; the other occurs near F; it is less strong but broader.

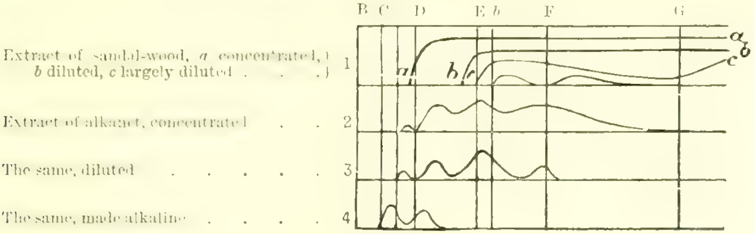


FIG. 7.

If to the solution in sulphuric acid some drops of sulphuric acid are added, containing 3 or 4 drops of strong nitric acid in 2,000 grms. of oil of vitriol, the colour becomes crimson. There is then formed a third band near D, whilst the two others diminish in intensity. The three bands appear with great strength if to a sulphuric acid solution of digitaline, some sulphuric acid containing $\frac{1}{3}$ p.c. of ferric chloride is added. These absorption spectra are visible several days after their production.

Delphinene, treated with strong sulphuric acid, gives a clear brown solution, exhibiting a band in the citron rays near D, and one-third towards E. The band becomes stronger by addition of a drop of bromine water, or better of sulphuric acid containing nitric acid, or of the solution of ferric chloride in sulphuric acid. The digitaline and delphinene spectra are quite different. The latter does not give a green reaction with hydrochloric acid.

Belladonnine. This alkaloid occurs in atropine imperfectly purified; it dissolves in sulphuric acid, to which it gives a yellowish colour. When heated the mixture takes a reddish colour. This colouration is characterised by a black band in the bluish-green near F, all other rays being transmitted. The thickness of liquid used for these tests is 5 mm. (C. Hock, C. R. 93, 849, 1881).

(9) **On the spectrum of blood and the detection of blood-stains.** The colour of blood is due to *hæmoglobin*, a compound of an albuminoid substance with *hæmatin*, a colouring matter containing iron. The colour of arterial blood is scarlet, while venous blood is dark-red, or purple, and in thin layers greenish. The former contains *oxyhæmoglobin*, the latter *hæmoglobin* free from oxygen. The absorption spectrum is characterised by two extraordinarily persistent bands, visible in a solution containing $\frac{1}{9700}$th of blood (fig. 8). When defibrinated blood is exposed to the air its colour changes to brown, and it acquires an acid reaction. The substance contained in it is called *methæmoglobin*; it is seen on the edges of healing wounds, and in old blood-stains. It may be produced by the action of *weak acids* on hæmoglobin, by the action of oxidising agents, such as ozone, and permanganates, and even by the hydrogen evolved from palladium charged with the gas.

Detection of blood-stains. If the stains are soluble in water, they are carefully washed out and the spectrum of the solution noted. The solution is then treated with ammonium sulphide or other reducing agent, and the change in the spectrum is again noted. If the stains are insoluble in water, they must be digested with a warm solution of sodium carbonate, 1 to 10 of water; the colouring matter dissolves and the spectrum is noted. Some ammonium sulphide is added, and two extraordinarily powerful bands of reduced hæmatine are developed. On shaking with air the liquid ceases to show them, but a further addition of the reagent causes them to return. *This reaction affords most important evidence for the recognition of blood in medico-legal cases* (fig. 8). As an example of its delicacy, it may be mentioned that a small spot of blood, between 1 and 2 mm. in diameter, which had dried up on a handkerchief for three days, was digested in 1 c.c. of dilute sodium carbonate solution. It gave a very slight greenish tinge, which in a tube 12 mm. in diameter showed no spectrum, but after warming with 2 drops of ammonium sulphide the marked band in the green between D and E appeared distinctly, and was visible both by daylight and gaslight when viewed with a pocket spectroscope 45 mm. in length and 10 mm. in diameter.

(Absorption spectra of hæmoglobin and derivatives, with both a prismatic scale and scale of wave-lengths, are figured in Wurtz's Dictionnaire-Supplément, art. 'Hæmoglobine,' p. 901.)

Reichardt asserts that fabrics dyed with indigo are capable of yielding a spectrum similar to that of blood if treated with warm potash solution, but H. W. Vogel and Gänge have shown that the absorption band of indigo differs from that of blood in position, behaviour, and character, for it becomes decidedly weaker and disappears completely when cold. At the same time, the colour of the liquid becomes green. Ammonium sulphide causes no change in this spectrum, provided the heating with concentrated alkali has been sufficiently prolonged.

2 c.c. of blood diluted to 20 c.c. heated with a few drops of caustic soda solution (sp.gr. 1·4) yields a green solution, which changes on cooling to reddish yellow. Indigo behaves in an exactly opposite fashion (fig. 9).

If the cold alkaline solution of blood be shaken with air, the band disappears, *but it returns with the greatest intensity* on treatment with ammonium sulphide; at the same time another band at E, *b* appears (Curve 4, fig. 9), and then the hæmatin spectrum discovered by Stokes appears. *This last change is decisive* (H. W. Vogel, 'Praktische Spectralanalyse').

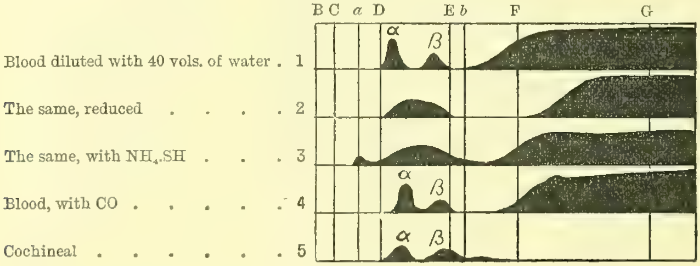


FIG. 8.

Photographed blood-spectra. Soret has observed three bands in the violet and ultra-violet region. With a dilution of 1 to 40 of water and a thickness of 3 to 4 mm. of liquid, electric sparks being the source of illumination, the first band falls upon Cadmium 12, wave-length 3260—this is probably due to hæmoglobin—the second occurs at Cadmium 17, wave-length 2747, and is caused by serine of the blood serum. With a dilution of 1 in 1000, with a thickness of 10 mm., a band is seen in the violet nearly filling the interval between G and H. Its centre falls on *h*. Diluted 1 to 600 it entirely fills the interval from G to H, and with 1 to 400 the band comes to the one side below G, and on the other to beyond H, all the ultra-violet being absorbed (L. Soret, 'Archives des Sciences Naturelles,' 10, 195).

It is obvious that by successive dilutions and measurements of the bands both at this end and at the less refrangible region of the spectrum, blood may be determined quantitatively.

(10) **Detection of carbon-monoxide poisoning.** Carbon-monoxide is readily absorbed by the blood. It causes the colour to become darker, and the position of the bands is nearer to the green. The separation of the bands is less distinct. *The spectrum of carbon-monoxide-hæmoglobin remains absolutely unchanged when treated with ammonium sulphide.*

Carbon-monoxide-hæmoglobin is charged with oxyhæmoglobin when poured several times from one glass to another, or if a little oxygen is passed through it; the spectrum will then undergo reduction by the usual process.

Wave-length measurements of absorption bands of blood-colouring matters calculated from the drawings of Preyer and of Hoppe-Seyler, by Dr. C. A. MacMunn.

Oxyhæmoglobin, or *Cruorin.*

	Wave-lengths, millionths of a millimetre
Hoppe-Seyler .	584–570, 547–527

Preyer, solution containing less than 0·01 per cent. of

	Millionths of a millimetre, one band
Oxyhæmoglobin . . .	583–573

Solutions containing	Millionths of millimetre, two bands
About 0·04 per cent. .	583–573, 547–532
0·09 „ .	583–572, 551–531
0·18 „ .	586–572, 551–529
0·37 „ .	589–568, 554–524

Between 0·6 and 0·7 per cent. .	590–564, 556–521
	One band
About 0·8 „ .	594–518
5·4 „ .	At this strength

absorption is so energetic that the only bright part of the spectrum is from 660 to 663.

Oxyhæmoglobin.

	Millionths of a millimetre
MacMunn . .	586–568·5, 555–526

Hæmoglobin, free from oxygen.

	Millionths of a millimetre
Hoppe-Seyler . . .	598–537
Preyer	594–538
MacMunn	592–534

Hæmatin, reduced hæmatin; hæmochromogen, in alkaline solution.

	Millionths of a millimetre
Hoppe-Seyler .	565–548, 533–513
Preyer . . .	566–549, 532–518

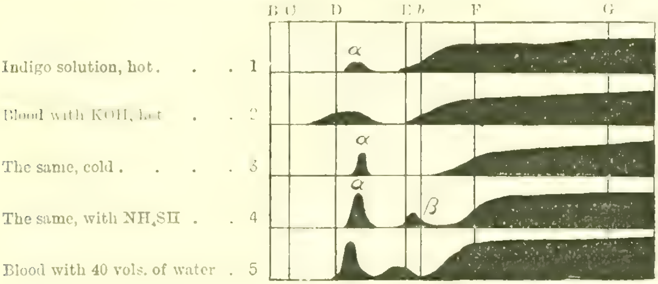


Fig. 9.

Carbon monoxide hæmoglobin.

	Millionths of a millimetre
Preyer . . .	583–564, 547–529
(*A stronger solution*)	583–561, 547–521

(Proceedings, Birmingham Philosophical Society, iii. 351, 1883.)

QUANTITATIVE ANALYSIS BY SPECTRUM-PHOTOMETRY.

Vierordt has described an instrument and method of working which enables us to determine the quantity of a substance in solution by determining the absorptive power which it exerts on definite rays of the spectrum. The upper and lower halves of the slit of the spectroscope can be enlarged or contracted independently of each other by two micrometer screws, which serve to measure the width of the apertures. There are thus two spectra superposed, the brightness of which can be modified at will. The brightness of the spectrum is proportional to the width of the slit—that is to say, to the quantity of light that passes through. If light traversing one-half of the slit be made to pass through an absorbing liquid, and the screws be so adjusted that both spectra are of the same brilliancy, then the relation of the width of the two halves of the slit will be inversely as the brightness of the two spectra. Unfortunately measurements made in this simple manner are not sufficiently exact for all photometric purposes, because when the slit is widened beyond a certain point the spectra cease to be pure, and further, by reason of diffraction, the whole of the rays which pass the slit are not completely utilised in forming the spectra. It is possible, however, to reduce the quantity of light which passes the slit without altering the width of the slit, first by introducing in the path of the rays one or more neutral-tinted glasses (Vierordt's method), or secondly, two spectra may be superposed, and the brightness of one may be decreased by the measured rotation of a Nicol's prism. This is the principle of the photometers of Bouguer, Foucault, and of Becquerel. Thirdly, two spectra are oppositely polarised, so as to be traversed by interference bands. These are disposed inversely, but they disappear if two spectra of the same brightness are superposed. This is the principle of instruments designed by Babinet, Desains, Wilde, and others.

Glan's spectro-photometer is an instrument of the former description which has been modified and improved by Crova. The spectra to be compared are separated by a band of darkness of variable width, which is produced by a triangular or wedge-shaped plate of brass which slides over the slit, the base of the triangle being parallel to the slit and its motion in a direction at right angles thereto. A double-image prism placed before the prism of the spectroscope doubles each of the two spectra into two others polarised at right angles. On shifting the triangular plate of brass which divides the slit into two, it is easy for the lower spectrum of the upper half to be applied exactly to the upper spectrum of the lower half, and these two are polarised at right angles. The other spectra may be hidden by a screen. If now a Nicol's prism is interposed between the slit and the collimator lens at a certain angle it will render the spectrum of the extraordinary ray equal in brightness to that of the ordinary ray.

Calling the angle of the principal sections of the Nicol and of the double-image prism α, and the intensity of the rays corresponding to the two spectra i and I, we obtain from the law of Malus $i \cos^2\alpha = \mathrm{I} \sin^2\alpha$, or $i = \frac{\mathrm{I} \sin^2\alpha}{\cos^2\alpha} = \mathrm{I} \tan^2\alpha$.

The intensity of one ray being constant, when we vary the other the new angle α' corresponds to another intensity $i' = \mathrm{I} \tan^2\alpha'$; the relative intensities i and i' are calculated from the squares of the tangents to the arcs α and α'.

The intensities of spectra may be compared with an approximation of from 1 to 2 per cent.

Spectro-photometers of the second kind are much more exact. In Trannin's instrument the slit is divided, as in other cases, into two, and either within or behind the collimator there are placed a Foucault's prism, a plate of quartz cut parallel to the optic axis, and a Wollaston's double-image prism. After passing through this train the prism of the spectroscope produces spectra showing interference bands running parallel to Fraunhofer's lines all through the spectrum. The double-image prism, however, not only assists in the production of the bands, but doubles the spectra into two others, which are oppositely polarised, and consequently the bands occupy alternate positions in the two spectra of the extraordinary and ordinary rays. The angle of the double-image prism can be cut to separate the images of the slit to such a degree that the lower part of the spectrum of the ordinary or less deviated ray, may be superposed on the spectrum of the extraordinary or most deviated ray.

In the part common to the two spectra, where the light is of equal intensity, the interference bands disappear. As the two spectra under comparison are one from the upper, the other from the lower half of the slit, they may come either from two sources or from the same source, and the rays from one of them may be made to traverse a solution. A variation in the distance of sources of light from the slit, if they are unequal, will render them equal. But the greatest precision is attained by introducing a Nicol's prism and rotating this. Angular measurement will, as in the previously mentioned case, give a mean value of the intensity of the two spectra. This method is ten times more accurate than that of Glan, but is applicable only to somewhat extended regions of the spectrum.

Gouy preferably produces the interference bands perpendicular to Fraunhofer's lines, and for this purpose he makes use of a Babinet's compensator, which receives the two lights to be compared and projects horizontal fringes upon the slit of the ordinary spectroscope. If the two lights are equal the two series of bands which are produced disappear in the spectrum. If one of the series is carried into a given region of the spectrum this region will be streaked horizontally with very visible fringes, even if the extent of the rays is very limited. The fringes may be made to disappear by the use of the compensator, and this, as in the preceding case, admits of a measure of intensity of the rays (Journal de Physique D'Almeida, vol. 5, p. 297; C. R. 83, 269).

Objections to other methods than that of Vierordt may be raised on the ground that there is a great loss of light, and that the apparatus is not so simple.

Quantitative analysis of coloured solutions.

This method gives very good results when the solutions are sufficiently strong in colour or give sufficiently strong absorption bands.

There are three ways of obtaining results: 1st, by direct comparison; 2nd, by determining the co-efficient of extinction; 3rd, in certain special cases, by the appearance or disappearance of certain bands.

1st. Supposing we have a solution of known strength, and it is required to ascertain the strength of a solution containing the same substance, we may use an instrument such as that of Glan or of Gouy, or only a simple direct-vision spectroscope with a total-reflection comparison prism fitted to the slit. The absorption spectra of the same thickness of the two solutions is compared. If they are not of equal brightness one may either dilute the stronger solution or increase the thickness of the weaker one. Thicknesses which produce the same degree of absorption are inversely proportional to the degree of concentration of the solutions. From this a simple calculation gives a mean.

Example.—A standard solution of known strength $\frac{a}{100}$ examined through a thickness of 3 centimetres produces the same absorption as a solution of unknown strength $\frac{x}{100}$ in a thickness of 7 centimetres;

$$\frac{a}{7}=\frac{x}{3}, \text{ hence } x=\frac{3}{7}a.$$

The standard solution $\frac{a}{100}$ would have to be diluted with b of water in order to yield the same amount of absorption as $\frac{x}{100}$.

Both solutions have now the same strength, that is to say, they contain: $\frac{a}{100+b}$; whence $\frac{a}{100+b}=\frac{x}{100}$ and $x=\frac{a\times 100}{b+100}$.

2nd. In cases where a standard solution is not available for comparison, spectro-photometry is most advantageous. We determine once for all the absorptive power for a given region of the spectrum which characterises each solution. The number which represents this is called by Bunsen its 'co-efficient of extinction.'

A light with intensity $=1$ is transmitted by an absorbent medium; after having traversed a thickness $=1$, it will be reduced to $\frac{1}{n}$; after passing through a second thickness the intensity will be

$$(1) \quad . \quad . \quad \frac{1}{n}\times\frac{1}{n}=\frac{1}{n^2};$$

after the action of a thickness x, it will be reduced to $\frac{1}{n^x}$, from which the intensity I of the remaining light will be $\mathrm{I}=\frac{1}{n^x}$, and $\frac{1}{\mathrm{I}}=n^x$; or by logarithms: $-\log \mathrm{I}=x\log n$.

$$(2) \quad . \quad . \quad \log n=-\frac{\log \mathrm{I}}{x}.$$

Let us call the co-efficient of extinction α; the reciprocal of the thickness after the intensity of the light has been reduced thereby to a tenth, *i.e.* for a thickness $\frac{1}{\alpha}$ the intensity $\mathrm{I}=\frac{1}{10}$; consequently we obtain $\frac{1}{10} = \frac{1}{n^{1:a}}$ or $10 = n^{1:a}$; or by logarithms

$$\log 10 = 1 = \frac{\log n}{a}$$

or again $\log n = a.$

But as we have seen, according to equation (2), $-\log \mathrm{I} = x \log n$, whence $-\log \mathrm{I} = ax$.

Let us now suppose that what has passed through thickness 1 is that which makes $x = 1$; the intensity which is 1 at incidence will be reduced to I, I being given by the formula $-\log \mathrm{I} = a$.

Whence we derive a second definition of the co-efficient of extinction; it is the logarithm of negative sign of the intensity after passing through a thickness 1, the intensity of the incident light being equally 1. From the first definition it follows that the co-efficient of extinction is inversely proportional to the thickness which produces a certain absorption, or *proportional to the concentration of the solution.* But it follows from the second definition that we can determine it in absolute values by a simple photometric measurement made with the spectrum photometer, and hence its importance.

Let us suppose that a light of intensity 1 is reduced to $\frac{3}{5}$ by the action of a liquid contained in a cell with a thickness of 1 centimetre; then $a = -(\log 3 - \log 5) = \log 5 - \log 3$.

We know that for solutions of the same substance a the co-efficient of extinction varies with the concentration, where, if c, c', c'', &c. express the quantity of colouring matter contained in the same volume of the solution, we get

$$a : a' = c : c' \text{ or } \frac{c}{a} = \frac{c'}{a'} = \text{constant A.}$$

Vierordt calls this the absorption ratio.

The constant A is easily deduced when a solution of known strength is prepared, and the co-efficient is optically determined. Then we obtain the value $\frac{c}{a} = \mathrm{A}$.

Example.—For instance, chrome alum, 1 c.c. of a solution contains 0·07176 grms. of salt, a thickness of 1 c.m. reduces the light from intensity 1 to 0·05.

$$\log 0{\cdot}05 = 0{\cdot}69897 - 2.$$

This as a negative becomes

$$a = 2 - 0{\cdot}69897 = 1{\cdot}30103$$

From which the constant

$$\mathrm{A} = \frac{c}{a} = \frac{0{\cdot}07176}{1{\cdot}30103} = 0{\cdot}05515.$$

If A be determined once for all it is a simple matter, from the observed co-efficient of extinction of another solution, and from the equation $\frac{c}{a} = \mathrm{A}$, to ascertain the strength c of the solution.

The quantity of salt in 1 c.c. = A × the co-efficient of extinction a.

Vierordt has determined the co-efficients of extinction for a number of substances, and applied his method to the purposes of technical chemical analysis and physiological chemistry, as, for instance, determining the decolourising power of animal charcoal, and estimating the quantity of blood in fluids from the hæmoglobin present. Elaborate tables are published in his work, 'Die quantitative Spectralanalyse in ihrer Anwendung auf Physiologie, Physik, Chemie und Technologie,' Tübingen, 1876.

Schulz's rectifier or corrector is a piece of flint glass with parallel plane ends and 1 cm. in length, which is placed in the cell with parallel sides of glass which are 1 cm. apart. If water alone is placed in the cell and the level of the liquid is even with the division of the upper and lower half of the slit, the spectrum obtained through the water is brighter than that which merely passes through the air. The normal brightness is obtained by looking through the glass corrector instead of through water, and if a coloured liquid is to be examined this is then poured into the cell. If instead of a coloured solution water be used, then both halves of the slit admit spectra of equal brightness (H. W. Vogel, 'Praktische Spectralanalyse').

(11) **The estimation of hæmoglobin in blood.** The instrument recommended is a modification of those used by Trannin and Violle for spectrum photometry. The cell containing the solution is divided into two in a direction at right angles to the slit. Between this and the slit is placed a double image prism and a polariscope. The double image prism (Wollaston) gives two images of each half of the cell, the ordinary image of the one being exactly applied to the extraordinary image of the other, so that the two spectra can be compared with precision. For this purpose the lime-light is recommended. The substance to be examined is placed in one cell and the standard of comparison in the other. By turning the Nicol, the two spectra are brought to the same brightness and the absorption of light is reckoned from the angle of rotation. The angle for a standard solution of hæmoglobin is once for all determined, all subsequent estimations being made against water.

Hæmoglobin treated with carbon monoxide shows no variation in absorptive power.

Determinations of the hæmoglobin in the blood of persons in various stages of disease are of great pathological value (E. Branley, A. Ch. [5] 27, 238-273; C. J. 44, 394, 1883).

(12) **The valuation of indigo samples.** Wolff accomplishes this by Vierordt's method, using the universal spectral apparatus made by Krüss of Hamburg, which has a slit with a symmetrical movement to both jaws in opening or shutting. A sample of indigotin, crystallised and in a state of perfect purity, was weighed out and digested in pure sulphuric acid for 24 hours, by which time it had dissolved.

A solution was so diluted that the known quantity of indigotin was 1 in 2000, or 1 c.c. contained 0·0005 grs. The region of absorption observed lay between C and D. Calling the degree of dilution a, the intensity of the light b, and the co-efficient of extinction c, observations were made with the solution of known strength.

Subsequently samples of various kinds of indigo were compared with the standard solution simply by determining a, b, and c.

(13) **Determination of the decolourising power of bone charcoal.** The decolourising power of commercial bone charcoal is very variable; its excellence determines its value. In order to estimate it, a given quantity of dilute syrup is shaken with a certain quantity of the charcoal, and an observation is made to ascertain how far

the liquid is brightened. Syrups absorb the blue and violet rays if coloured, and a great difference is noticeable in the brightness of the spectrum in this region, if but a slight difference characterises their colour. It is of no consequence how much substance communicates the colour, because the proportional quantities of colouring matter are strictly compared. Vierordt observes the blue from F to a point towards G, and excludes from the field of vision other portions of the spectrum.

Examination of feebly-coloured syrup.—If the chosen region of the spectrum between F and G appears fairly bright the syrup need not be diluted. The upper half of the slit is then closed until the spectrum is of the same brightness as that from the light of a paraffin lamp after passing through the absorbing liquid. The micrometer screw head is then observed, and the reading should show that the remaining intensity of the rays is 0·25. The screw head being divided into 100 parts, the third place of decimals is easily read by judgment. The mean of 6 to 10 rapid readings serves to fix the number with sufficient accuracy to 3 decimal places.

In Vierordt's table of co-efficients of extinction (negative logarithms of bright intensity) the number 0·60206 stands opposite 0·250. This number yields the relative quantity of colouring matter in the syrup, which is proportional to the co-efficient of extinction.

If the absolute amount of colouring matter is unknown, Vierordt describes this quantity, if the light is diminished by one-tenth of its original brightness, by 1. The table gives only those readings which lie between 80 and 10 divisions of the micrometer, or ·8 and ·1, and their values in colouring matter, which is sufficient for all practical purposes.

It is not advisable to diminish the slit more than one-sixth of its width—that is, to less than 15 divisions. It is better, in case the colour is strong, to double the width of the lower slit, and to divide the readings of the upper one by 2. Darkly-coloured syrup is diluted with 3 volumes of distilled water. If the excess of light is found to be 0·273, the proportional quantity of colour (or co-efficient of extinction in Vierordt's table), 0·56384 is multiplied by 4, which gives the true quantity of colour in the undiluted syrup as 2·2555. The colour is a guide to the necessary dilution.

With very feebly-tinted liquids a greater thickness, say 2, 4, or even 6 c.m. of liquid, are observed. If, for example, 4 c.m. are examined, and the comparison of both spectra indicates an excess of light equal to 0·56, then in the table the number found is 0·25182, and this must be divided by 4 or $\frac{0{\cdot}25128}{4} = 0{\cdot}0629$ in order to ascertain the quantity of colour.

Determination of the decolourising power of charcoal.—The liquid must be clear, and of such a colour that 1 cm. admits of half the green rays being recognised. Dilute with about 3 volumes of water, and prepare a sufficiently large quantity to serve for a considerable number of tests, and call this the 'test solution.' A measured volume of the test solution is diluted to one-eighth or one-sixteenth, and the quantity of colour is determined therein; this, if multiplied, the dilution 8 or 16, gives the strength of colour of the test solution.

Thus three experiments were made with a solution, and the following numbers were obtained.

Dilution of solution	Intensity of spectrum or absorption co-efficient	Quantity of colour by reference to table	Calculated colour in the test solution
$\frac{1}{8}$	0·205	0·688	0·688 × 8 = 5·404
$\frac{1}{16}$	0·46	0·337	0·337 × 16 = 5·392
$\frac{1}{32}$	0·68	0·167	0·167 × 32 = 5·344

Mean of these determinations, 5·380.

Testing the charcoal.—10 c.c. of the test solution are shaken with 3 grms. of the charcoal for one minute, and filtered through pure filter paper. The quantity of colour is then determined, and the difference between this and that in the test solution which was determined is a measure of the decolourising power of the charcoal.

Example.—A test solution, containing 5·38 of estimated colour, was shaken with 3 grs. of finely-powdered, purified bone charcoal and filtered. The absorption spectrum of the filtrate gave an intensity of 0·39, which in the table indicates a quantity of colour equal to 0·4089. The colour absorbed by the charcoal is

$$5{\cdot}380 - 0{\cdot}4089 = 4{\cdot}891,$$

that is to say, the proportion is $\frac{4{\cdot}891}{5{\cdot}380} = 0{\cdot}909$, or in round numbers 90 p.c. of the colouring matter. After treatment with charcoal it will reach beyond G and towards H.

Vierordt has observed that the colour remaining in the test solution is inversely proportional to the charcoal used, but the mode of treatment and length of contact with the charcoal varies the effect, even where the same quantity of material has been employed (H. W. Vogel, 'Praktische Spectralanalyse').

(14) **The determination of nitric acid in water analysis, &c.** When a solution of diphenylamine in sulphuric acid is brought into contact with nitric acid or a nitrate, a blue colour results, and, other conditions being the same, the intensity of the colour depends upon the amount of nitric acid present. The absorption spectrum is also constant for a given depth of colour. The co-efficient of extinction of such a solution having been once determined, the amount of nitric acid may be calculated from a single observation (Settegast, A. Ch. [7] 7, 243–271). By a similar process phosphoric acid is determined.

(15) **Application of the spectro-polariscope to sugar analysis.** Many persons fail to become expert operators with the saccharimeter because they are incapable of distinguishing changes from the transition tint so nicely as a close reading of the scale requires. Readings are made with great rapidity and fair accuracy in the following manner.

Adjust a Scheibler saccharimeter to zero, and insert before the eye-piece a pocket spectroscope, with the slit horizontal, or at right angles to the line bisecting the chromatic field. Looking in then through the spectroscope, and focussing the eye-piece of the saccharimeter and of the spectroscope, two vertically-disposed parallel spectra will be seen separated by a well-defined black line, which is the image of the line mentioned. The spectra will resemble ordinary white-light spectra, except that a narrow, intense absorption band will appear across both of them near D. The least turn of the screw will destroy the coincidence of the two absorption bands, one moving upward and the other downward, and a sufficient revolution of the reading screw will cause one to pass out to the infra-red and the other to the ultra-violet, the spectra otherwise being practically unchanged. To determine the percentage of sugar in a sample by this method, bring the two absorption bands to coincidence and insert the tube of sugar solution, which will throw the bands out of coincidence precisely as if the screw had been considerably turned. Bring the bands to coincide again by means of the reading screw, and the scale will give the percentage required.

When the sugar solution is examined multiple spectra may make their appearance, but no confusion need arise if only the two middle spectra be observed (W. G. Levison, Am. S. 24, 469, 1882).

Spectrum Photography.

Eye observations of spectra are applicable chiefly to those rays which are clearly visible, and therefore it has been found advantageous to employ photography for the purpose of observing the very extensive ultra-violet region. The character of a photographed spectrum depends: first, on the optical train, whether of quartz or of glass; second, on the nature of the sensitive film on the photographic plate; third, on the period of exposure; and, fourth, the rate of vibration of the emitted rays. Generally speaking, a photographed spectrum is a permanent record of a chemical reaction distributed in time and space. It is, in fact, a series of as many observations as there are lines in the spectrum photographed. In photographing spectra ranging from 4,000 to 2,000 tenth-metrets, the most suitable prisms are of quartz, such as were first used by M. Cornu; they are cut perpendicular to the axis, one being of right-handed, the other of left-handed, rotation, and each with an angle of 30°, and in section shaped thus + ◺ ◿ −. They may be cemented back-to-back with a drop of glycerine, or the one may be fitted to the collimator close to the lens, the other in a similar manner in front of the telescope or camera lens. The lenses are of similar thickness, and of right- and left-handed crystals. Instead of a telescope a photographic camera of somewhat unusual construction is employed, the plate carrier of which is so inclined to the direction of the mean ray of the spectrum that it makes an angle therewith of 19-24° (fig. 10). By such means all the rays, inclusive of the wave-lengths given above, are focussed with accuracy on one plate, and a magnifying power of 25 diameters may be employed with advantage in examining the photographs. The camera back is constructed so that the normal position is angular, but it is also made to swing on a vertical pivot situated at its centre, the centre of the pivot being in the same vertical plane as the centre and front of the surface of the focussing screen. The collimator should be fitted with a graduated draw-tube and rack and pinion. A connection between the back and the front half of the camera is made of leather, folded bellows fashion. This admits of a certain degree of 'side-swing,' with to and fro motion for focussing. The camera should be mounted on an iron frame, which falls into position on an iron table to which the collimator is fixed. No matter what be the length of the collimator, it should be supported for at least one-half of its length, and admit of being fixed at the minimum angle of deviation for the mean ray. An opening is cut in the collimator tube of about one-third of its circumference in width, and two inches in length, which may be closed by a sliding cover. This enables the experimenter to judge in which direction to move the electrodes, so that the rays of the spark may fall exactly upon the slit and pass along the axis of the collimator. This is done by means of a card, which fits just inside the opening, and has a vertical line ruled at a point coinciding with the centre of the tube. When the spark is properly adjusted, a spindle-shaped bundle of rays strikes the centre of the card. The slit should be $\frac{1}{500}$ to $\frac{1}{1000}$ of an inch in width, and it is well to protect it from dust by a plate of quartz. The source of illumination, if absorption spectra are to be studied, should be condensed sparks from metals affording lines of known wave-lengths, and so numerous that they practically serve the purpose of a continuous spectrum.

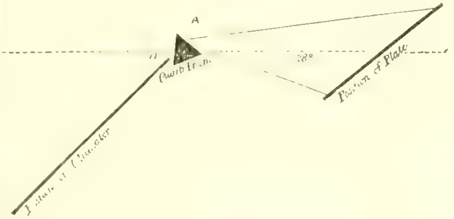


Fig. 10.

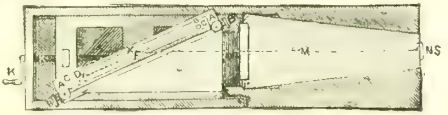


Fig. 11.

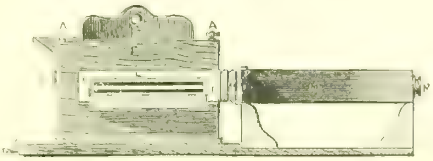


Fig. 12.

Details of construction of the camera will be understood from figs. 11 and 12, which show the instrument in plan and elevation, while fig. 13 shows the back of the camera with the dark slide in position, but with the back spliced and the shutter in front slightly raised. The two portions of the body are shown in this case to be supported on a wooden stand instead of the metal table.

M is a rigid shallow box, in front of which is the lens in its fitting, N. L, which is a continuation of M, is triangular in form, and is movable in two directions. It moves to and fro by means of the screw K, and makes a greater or lesser angle with the mean ray X—N by turning on the pivot situated at X. The screws A A serve to clamp the 'swing back' in position. The camera back is constructed to carry plates capable of taking several photographs, and the dark slide is moved up or down by the thumb screws B B acting on a pinion, which works the rack on the front edge of the dark slide D D (fig. 13). C C is the movable frame for the dark slide. The interior edge of the dark slide is shown in shadow by G G, while H is the slit in the camera back through which the spectrum is projected. E and F represent the door at the back, and the sliding front of the dark slide respectively. In the elevation is an opening, I I, fig. 12, in the body of the camera, and door to the same, J, through which is seen the slit H, by which the spectrum passes to the sensitive plate. In the act of focussing a glass plate covered with some fluorescent material is placed in the dark slide, and the lines of the spectrum are viewed through I I by reflection.

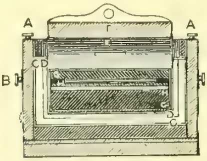


FIG. 13.

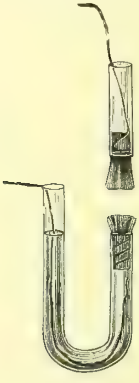


FIG. 14.

Some care is required to secure a proper adjustment of the instrument and obtain good photographs. The battery power, size of coil, and condensing surface must all be proportional to the distance between the electrodes, in order that the rapidity of the passage of the sparks should render the light almost continuous. The coil should give a six-inch spark in air, and it is better to excite it with three storage cells than with five cells of Groves battery. The electromotive force of the cells should be 1·8 volts. The current required to work such a coil is from $7\frac{1}{2}$ to 8 ampères; three storage cells yield $15\frac{1}{2}$ ampères, but with a resistance of $\frac{1}{4}$ of an ohm in circuit the current is conveniently reduced. Electric light carbons have been used for the resistance. The smallest condenser to be of any use has 72 square inches of tin-foil on each side of a plate of glass and a margin of three inches. It is fixed in a wooden frame with binding screws attached to the wood. Special methods are adopted for examining the emission spectra of solutions and for observing absorption spectra. Two materials have been commonly used for solutions—namely, electrodes of gold and of graphite. Wicks of gold wire are made to pass just above the surface of the solution, which is contained either in a porcelain crucible or in a small U-tube, one limb being longer than the other (fig. 14). Graphite electrodes for the same purpose are cut to the shape of wedges, about $\frac{1}{4}$ inch in length and $\frac{1}{8}$ in width. The wedges are attached to platinum wires, and are fixed in glass tubes, as shown in the figure; the lower wedge dips into the solution, which is carried to its upper edge by deep grooves or scratches. Capillary attraction keeps the lower electrode moist at its upper surface. Generally speaking, there are only two lines of any other element than carbon visible in the spectrum of good graphite, and these are the first and third of the quadruple group in the magnesium spectrum, wave-lengths 2794·4 and 2801·1. The second and fourth are very faintly seen, wave-lengths 2796·9 and 2789·6. Impure graphite is apt to show the spectrum of iron.

In order to secure fine definition, a condensing lens in front of the slit is necessary. It should be of quartz, of three inches diameter and three inches focal length. The spark is best if very brilliant and not exceeding three-sixteenths of an inch in length. It should pass upwards—that is to say, the lower electrode must be the negative pole; when this is the case splashes of liquid are carried up and the noise of the spark is louder. The best gelatino-bromide emulsion plates are used for photographing. The image is developed by pyrogallol or hydroquinone and ammonia. Hydroxylamine hydrochlorate, and caustic soda with a little potassium bromide is also a good developer. Comparative exposures should be made with electrodes of cadmium.

The following established facts regarding ultra-violet spark spectra form the basis of all the practical applications of spectrum photography:

1. When carbon or metallic electrodes, which emit short lines, are moistened or partially immersed in water, the short lines are lengthened.

2. The impurities in a metal, or the minute constituents of an alloy, generally appear as spectra of short lines. When both electrodes are of the same material, the impurities appear at one electrode, the negative pole only, but when the proportion of the impurity or alloy is increased, the long lines are seen as short lines at both poles, a further increase in proportion bringing them out as long lines.

3. Of the non-metallic elements, boron, carbon, and silicon exhibit line spectra.

4. The spectra of carbon and silicon may be detected in photographs taken from metallic electrodes, such as those of very pure iron wire.

5. Insoluble compounds which are not volatile do not yield spark spectra. Insoluble but somewhat volatile compounds, such as thallium chloride, yield a feeble spectrum of metallic lines.

6. With the exceptions of boron and silicon, the non-metallic constituents of a salt do not affect the spark spectra of its solutions.

7. Solutions of metallic salts yield spectral lines identical in number and position with the

principal lines of the metals. Some of the short lines become long lines and very short lines do not appear, but whether the spectra are produced by metallic electrodes or solutions their character is identical.

8. The effect of diluting solutions of metallic salts is, first, to weaken and attenuate the metallic lines, and then, with a more extensive dilution, to shorten them until they finally disappear.

9. Accidental differences in the passage of the spark do not cause sensible variations in spectra obtained from the same substances, under any ordinary circumstances.

10. Spectra of metallic electrodes and of solutions are liable to the presence of the lines of calcium at wave-lengths 2967·3 and 3933, also occasionally, at 3736·5 and 3705·3. These, like yellow sodium lines, are caused by dust in the air.

Metallic electrodes are best shaped like those of graphite (fig. 14); they should be filed smooth at the edges. Globules of metal obtained by the blow pipe are flattened under the hammer only; they are held in screw clips pointed like drawing pens.

Absorption spectra of solutions are examined in a series of cells with quartz sides, measuring 25 mm., 20 mm., 10 mm., 5 mm. 4 mm., 3 mm., 2 mm., 1 mm. in thickness. The sides are not cemented, but pressed by clips against the cell, so as to be water-tight. Dipping the cells in melted paraffin in some cases is found sufficient to fasten them, but of course no liquid likely to dissolve the substance can be put into them.

The rays used to determine the absorption spectra of liquids are obtained by passing the spark between electrodes, one of which contains lead with 25 per cent. cadmium, the other tin with a similar proportion of cadmium. There being cadmium in the two alloys, the lines of that metal are continuous from pole to pole, while those of tin and lead stretch half across; they thus become easily recognised.

When the spectrum of an alloy, metallic precipitate, or solution has been photographed, sometimes, on account of the complexity of composition of the alloy, precipitate, or solution, or owing to the preponderance of one of the constituents, it is not easy to determine what substances are present and what are absent, even when the spectra of the substances sought for are well known. It is necessary in such cases to proceed according to one of the following two methods, or even to have recourse to both of them.

(*a*) *Method of identifying the elements by lines photographed from a known specimen.* A series of photographs taken from metallic electrodes and from solutions when the apparatus is properly adjusted should always be kept for reference. A substance may then be readily identified even when the wave-lengths of its lines are unknown, by super-position of one photograph upon the other, film to film, since there are but very few cases of actual coincidences of lines of similar character. On the small photographs from which copies were printed by the Woodbury process for publication in the C. J. xli. 90, it is easy to distinguish with a hand magnifier lines differing in wave-lengths by only two-tenth metrets, and, of course, with a microscope and a two-inch objective the examination of the actual plates is much easier. Having examined the photograph for all the elements which may possibly be present in the spark, if there be still some lines the presence of which cannot be accounted for, it is necessary to proceed according to the next method.

Reference lines used in the construction of an interpolation curve.

Scale numbers; Hundredths of an inch	Wave-lengths	Origin of lines	Reciprocals	Scale numbers; Hundredths of an inch	Wave-lengths	Origin of lines	Reciprocals
17	4480	Mg	2232	190	2812	Sn	3556
17·7	4454	Ca	2245	192·5	2801	Pb	3571
18·9	4434	Ca	2255	197	2778	Sn	3599
20·0	4424	Ca	2260	203·5	2747	Cd	3640
20·5	4414	Cd	2265	213	2705	Sn	3696
22·5	4386	Pb	2280	223	2662	Pb	3756
30·5	4245	Pb	2355	235	2613	Pb	3827
42·7	4061	Pb	2462	240	2593	Sn	3856
62·0	3800	Sn	2503	244	2576	Pb	3882
67·3	3739	Pb	2674	245	2572	Cd	3888
72	3683	Pb	2715	245·5	2570	Sn	3891
76·3	3639	Pb	2748	247	2561	Pb	3904
79	3610	Cd	2770	251·5	2545	Sn	3929
82·7	3572	Pb	2799	266·5	2495	Sn	4008
93·7	3465	Cd	2886	270	2483	Sn	4027
97	3437	Air	2909	272	2475	Pb	4040
101	3403	Cd	2938	281·3	2445	Pb	4090
106·5	3352	Sn	2983	282	2443	Pb	4095
109·5	3330	Sn	3003	286·5	2429	Sn	4116
115	3283	Sn	3045	289	2422	Sn	4128
118	3262	Sn	3065	295	2402	Pb	4163
119·5	3260	Cd	3067	298	2393	Pb	4178
129·5	3174	Sn	3150	306	2368	Sn	4223
135	3137	Pb	3187	311	2355	Sn	4246
151	3033	Sn	3297	318	2335	Sn	4282
155	3008	Sn	3324	320	2329	Cd	4293
159·5	2980	Cd	3355	322·7	2321	Cd	4308
165	2949	Pb	3391	325·7	2313	Cd	4323
171	2912	Sn	3434	335	2288	Cd Sn	4370
177	2880	Cd	3472				
178·5	2872	Pb	3481	344	2265	Cd	4415
180	2862	Sn	3494	351	2247	Sn	4450
182·5	2849	Sn	3510	353·5	2241	Cd	4462
185	2837	Sn	3524	368·5	2205	Pb	4535
186	2832	Pb	3531	372·5	2195	Cd	4555
188	2822	Pb	3543	395	2145	Cd	4662

(*b*) *Method of identifying lines when comparison spectra are not available.* By chemical processes of separation, it is of course easy to ascertain what metals may be looked for. The wave-lengths of the unrecognised lines must then be ascertained from an interpolation curve, and this curve may be constructed from measurements made directly from the photographs by means of an ivory scale with a bevelled edge, the divisions on the scale being hundredths of an inch. With a strong magnifier we may read by judgment to tenths of each division—that is to say, to thousandths of an inch. The best form of magnifier is one made like the compound eye-piece of a microscope, which is brought very close to the surface of the scale and photograph, so that false readings caused by parallax are avoided. It is most convenient if there are cross hairs or fibres of cocoon silk in the eyepiece. The preceding lines afford convenient points for drawing the curve. The scale numbers are of course arbitrary, the zero being fixed at any part of the spectrum where the plates cease to be sensitive. The reciprocals, which represent oscillation-frequencies in unit of time, yield a curve which more nearly approaches to a straight line than the curve of wave-lengths.

Fractions of a tenth-metret have been omitted from this list. The more correct numbers are to be found in the Phil. Trans. vol. clxxv. p. 49, part i. 1885, where also the scale numbers are given which refer to photographs published in the C. J. xli. 84, 1882. The object of these numbers is to facilitate the identification of lines, and this is further aided by a description of each line. See also Phil. Trans. clxxv. 325, Part ii. 1885.

Having pricked off on the photograph all the lines which have been recognised, or *vice versâ*, the scale is very carefully adjusted so that it gives correct readings with lines of known wavelength at different parts of the spectrum, as, for instance, with Nos. 9, 10, 11, 12, 17, and 25 of cadmium.

In order to adjust the scale accurately, it is convenient to rule a line down the whole of the spectrum, and this can be done by placing a very fine wire across the slit, about one-fourth or one-third the length of the spark, above the edge of the lower electrode; the edge of the scale should coincide with this line. Another way of effecting this is to make a slight nick in the edge of the slit plate; the line in the first case is clear glass, but in the second it is a dark line, by reason of the slit being wider at this point. For the most part it is a continuous spectrum showing strong lines reversed.

The scale numbers of the unrecognised lines are then read off, the curve is referred to, or the wave-lengths are recorded after reference to a tabûlated statement of scale numbers, and corresponding wave-lengths derived from readings on the curve. From maps or descriptions of spectra of the elements the corresponding lines are selected. The operation is performed more readily than it can be described. Having nothing to guide the observer but the position of the lines on the photograph and the wave-lengths deduced therefrom, it is particularly necessary to be guarded against the possibility of coincident lines or nearly coincident lines being mistaken. Any difficulty of this kind may be easily obviated if attended to.

(16) **Test for the purity of alcohol.** If a cell with quartz sides about 20 mm. or ¾-in. thick, be filled with the alcohol, photographs of the ultraviolet spectrum of cadmium as far as 2020 or 2030 should be obtained after interposing the cell in the path of the rays. Should the spectrum be short the spirit may be submitted to fractional distillation, and successive fractions examined until the portions containing the absorbing substances—such as amylic alcohol, essential oils, and aromatic substances—are isolated. By taking photographs of these fractions contained in cells of different thicknesses, varying from 5 mm. to 1 mm., and also by diluting the fractions with optically pure alcohol, the absorption bands characteristic of aromatic substances may be rendered visible. By this method aromatic substances have been found to occur in old Highland whisky, a characteristic absorption band appearing between wave-lengths 3260 and 2995 (Hartley, Cantor Lectures on Fermentation and Distillation, p. 25, published by the Society of Arts, 1884).

(17) **The examination of essential oils.** Essential oils are articles of great commercial value, and consequently are subject to adulteration. For the most part their chemical constitution is that of isomeric hydrocarbons, which may be divided into three polymeric groups corresponding to the three formulæ:—

(1) $C_{10}H_{16}$. (2) $C_{15}H_{24}$. (3) $C_{20}H_{32}$.

To the first-class belong the hydrocarbons derived from turpentine, orange, nutmeg, myrtle, and several others. The second group includes the hydrocarbons from rosewood, cubebs, calamus, cascarilla, patchouli, and cloves. The third group is represented by colophene. The optical characteristics of these hydrocarbons are as follows:

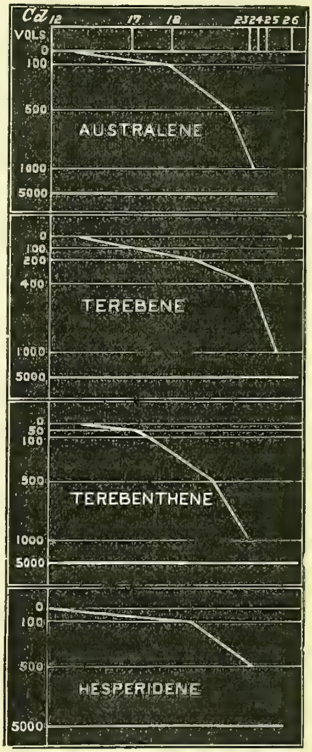


Fig. 15.—Isomeric Terpenes.

Showing the rays transmitted through 15 mm. of liquid after dilution with various proportions of alcohol. The ordinates represent the proportions of alcoholic solution containing one volume of the terpene.

1. Terpenes, with the composition $C_{10}H_{16}$, possess in a high degree the power of absorbing

the ultra-violet spectrum, though they are inferior in this respect to benzene and its derivations.

2. Terpenes, with the composition $C_{15}H_{24}$, have a greatly increased absorptive power.

3. Terpenes and their oxygenated derivatives always transmit continuous spectra; the spectra of isomers differ as to the magnitude of wave-lengths of the rays absorbed, and variations are observed on dilution (fig. 15).

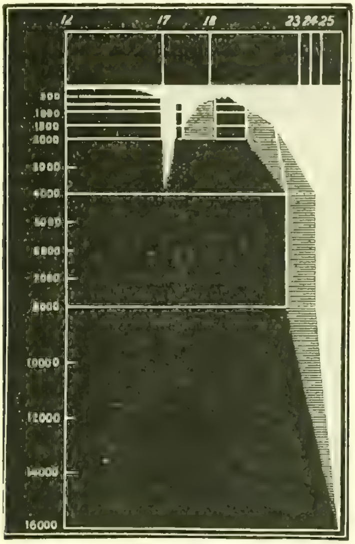


FIG. 16.

Hydrocarbon from oil of thyme (b.p. 162–163 C.), containing about 12 p.c. of cymene.

Some essential oils, when in a state of purity, are entirely composed of benzene derivatives; others are mixtures of benzene derivatives with terpenes. Of the former may be mentioned oil of bitter almonds, aniseed, wintergreen, and meadow-sweet, which are composed of benzoic aldehyde, anethol, methyl salicylate, and salycylol respectively. Of the latter, oil of bay, otto of pimento, and oil of cloves contain eugenol; nutmeg contains myristicol, peppermint menthol, carraway carvol.

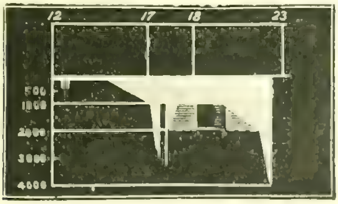


FIG. 17.

Hydrocarbon from oil of [illegible], showing the absorption bands due to cymene.

(18) **The estimation of cymene in essential oils.** Certain oils, which are essentially terpenes, as oil of lemons, sometimes contain cymene. Oils of orange, lemon, French and Russian turpentine have been described as containing as much as 8 p.c. of cymene; it has even been asserted that some oils consisted almost entirely of cymene, or were converted by the process of distillation into that substance. Cymene exhibits a narrow and very persistent absorption band at Cd 17 (figs. 16 and 17); it is shown when 1 volume is diluted with 2000 of alcohol, and is persistent until a dilution of 1 in 20,000. By photographing essential oils in different stages of dilution with optically pure alcohol, it was found that the oils of orange and of French turpentine alluded to contained no cymene, the Russian oil might have contained 4 p.c., and that some other hydrocarbons of essential oils contained very small quantities of cymene. One volume of cymene in 100 of essential oil is very easily detected. The purity of essential oils may be readily ascertained, and their value may in some cases at least be determined, by estimating the amount of impurity.

(19) **The identification and estimation of the alkaloids.** The greatest interest attaches to the examination of the alkaloids, because the absorption spectra offer so ready and valuable a means of ascertaining the purity and establishing the identity of the alkaloids. The differences in character of the various specimens of aconitine are remarkable; the comparatively harmless base is easily distinguished, and of those which are physiologically active, each has its distinctive absorption curve, so that each preparation may be absolutely identified. The cinchona alkaloids show strikingly distinct curves; so likewise do those of the papaveraceæ. Two specimens of morphine exhibit the same curve, and so do two of codeïne. There is a difference but yet a similarity between the morphine and the codeïne, which arises from the constitution of the two bodies being only slightly different, codeïne being a methyl-morphine.

ABSORPTION SPECTRA OF THE ALKALOIDS.

Measurements of absorption bands in tenth metres:

English aconitine. 0·1 grms. in 20 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
2 mm. .	3008–2747	Spectrum weak
1 mm. .	2978–2872	

The same solution diluted ten times, 0·01 in 20 c.c.:

5 mm. .	2995–2735	
4 mm. .	2965–2863	

Japaconitine. 0·1 grm. in 20 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
3 mm. .	2799–2614	Spectrum strong
2 mm. .	2747–2614	
1 mm. .	2747–2614	Absorption feeble here

Pseudaconitine. 0·1 grm. in 100 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
3 mm. .	3028–2431	Less refrangible part of spectrum strong
2 mm. .	2747–2504	

Aconitine (Morson's). 0·1 grm. in 100 c.c. alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
3 mm.	Band (1) 3033–2836	Spectrum well marked
	Band (2) 2740–2424	
2 mm.	Band (1) 3002–2863	
	Band (2) 2740–2424	

Aconitine. 0·1 grm. in 20 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
4 mm.	2863–2613	Spectrum well marked
3 mm.	2740–2658	

Quinine. 0·01 in 10 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
3 mm.	3403–3033	Well-marked spectrum
3 mm.	Band (1) 3403–3033	The second band is the weaker
	Band (2) 2974–2854	

Quinine sulphate. 0·01 grm. in 10 c.c. of alcohol, sp.gr. 0·8, and 5 c.c. of double normal sulphuric acid:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
5 mm.	3746–2865	A strongly-marked spectrum
4 mm.	3746–2875	
3 mm.	3691–3028	
2 mm.	3606–3466	

Cinchonine. 0·01 grm. in 10 c.c. of alcohol, sp.gr. 0·8, and 5 c.c. of double normal sulphuric acid:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
5 mm.	3465–2735	A strongly-marked spectrum
4 mm. & 3 mm.	3356–2835	
2 mm.	3260–2860	
1 mm.	3260–3022	

Quinidine sulphate. 0·01 grm. in 10 c.c. of alcohol, sp.gr. 0·8, with 5 c.c. of double normal sulphuric acid added:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
5 mm.	3737–2867	A strongly-marked spectrum
4 mm.	3690–2875	
3 mm.	3691–2891	
2 mm.	3178–3022	
1 mm.		

Cinchonidine sulphate. 0·01 grm. in 10 c.c. of alcohol, sp.gr. 0·8, with 5 c.c. of double normal sulphuric acid added:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
5 mm. & 4 mm.	3364–2860	A strongly-marked spectrum
3 mm.	3348–2860	
2 mm.	3258–2864	
1 mm.	3258–2907	Absorption incomplete here.

Morphia. 0·1 grm. in 25 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
2 mm.	2980–2660	A well-marked spectrum
1 mm.	2956–2747	

The same, 0·1 grm. in 10 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
5 mm.	2980–2747	A well-marked spectrum
4 mm.	2949–2838	
3 mm.	2949–2870	,,

Morphia. 0·1 grm. in 25 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays
3 mm.	3008–2613
2 mm.	2980–2613
1 mm.	2980–2836

The same solution, diluted to four times its volume, equivalent to 1 in 1000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
4 mm.	2980–2836
3 mm.	2980–2857
2 mm.	2980–2810

Tetracetyl-morphia. 0·1 grm. in 20 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays
3 mm.	2926–2572
2 mm.	2902–2610
1 mm.	2864–2745

The same, 0·1 grm. in 100 c.c. of alcohol, equivalent to 1 in 1000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
5 mm.	2964–2601
4 mm.	2821–2735

Codeïne. 0·1 grm. in 20 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays
2 mm.	2977–2612
1 mm.	2977–2747

The same, 0·01 grm. in 10 c.c. of alcohol = 1 in 1000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
4 mm.	2965–2735
3 mm.	2942–2798
2 mm.	2942–2863

The same, 0·1 grm. in 10 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays
2 mm.	2964–2660
1 mm. Band (1)	2747–2572
Band (2)	2962–2747

The same, diluted to five times its original volume, or to 1 in 500 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
5 mm.	2962–2747
4 mm.	2976–2747
3 mm.	2976–2747
2 mm.	2976–2740

Diacetyl-codeïne. 0·1 grm. in 10 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays
2 mm.	2947–2613

The same solution diluted five times = 1 in 500 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
5 mm.	2976–2609
4 mm.	2942–2740
3 mm.	2942–2740

Thebaïne. 0·1 grm. in 100 c.c. of alcohol, sp.gr. 0·8 = 1 in 1000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
2 mm.	3171–2568
1 mm.	3171–2568

The same solution diluted five times = 1 in 5000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
5 mm.	3171–2568
4 mm.	2976–2740
3 mm.	2976–2863

Papaverine. 0·1 grm. in 1000 c.c. of alcohol, sp.gr. 0·8 = 1 in 10000:

Thickness of liquid	Wave-lengths of absorbed rays
1 mm.	2546–2343

The same solution diluted five times = 1 in 50000:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
4 mm.	2545–2313	Ill-defined band
3 mm.	2545–2313	,,
2 mm.	2545–2313	,,
1 mm.	2545–2313	Band still visible

Narcotine. 0·1 grm. in 100 c.c. of alcohol, sp.gr. 0·8 = 1 in 1000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
4 mm.	3330–2707
3 mm.	3262–2839
2 mm.	3262–2829

Apomorphine hydrochloride. 0·1 grm. in 500 c.c. of alcohol, sp.gr. 0·8 = 1 in 5000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays	Remarks
2 mm.	2976–2568	This solution will not keep

Veratrine. 0·1 grm. in 20 c.c. of alcohol, sp.gr. 0·8:

Thickness of liquid	Wave-lengths of absorbed rays
2 mm.	3034–2848
1 mm.	3016–2860

The same solution, 0·1 grm. in 100 c.c., 1 in 1000 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
5 mm.	3008–2847
4 mm.	2976–2869

Cevadine. Merck's veratrine shows no absorption bands.

Brucine. Solution in alcohol, sp.gr. 0·8, 1 in 5000 c.c.:

Thickness of liquid		Wave-lengths of absorbed rays
5 mm.	Band (1)	3171–2857
	Band (2)	2793–2424

Remarks.—Strongly marked spectrum.

4 mm.	Band (1)	3171–2869
	Band (2)	2740–2568

Remarks.—This band is feeble.

Strychnine. Solution in alcohol, sp.gr. 0·8, 1 in 2500 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
3 mm.	2740–2310
2 mm.	2740–2310
1 mm.	2568–2427

The same solution diluted five times = 1 in 12500 c.c.:

Thickness of liquid	Wave-lengths of absorbed rays
5 mm.	2568–2427

Piperine. Solution in alcohol, sp.gr. 0·8, 1 in 5000 c.c.:

Thickness of liquid		Wave-lengths of absorbed rays
3 mm.		3600–2740
2 mm.	Band (1)	3600–2740
	Band (2)	2568–2310

Remarks.—The absorption is not quite perfect, one or two strong lines being faintly transmitted at 2427 and 2418 (Hartley, Tr. 176, 471, part ii. 1885).

II. Emission Spectra.

Some substances emit rays which are easily observed by the eye, because they are brilliantly coloured and are obtainable at low temperatures, but other substances present much more characteristic spectra at high temperatures and in the ultra-violet region. Photographed spectra of most of the metals are, on this account, of much greater interest than those in the region of visibility.

Owing to the spectra being the aggregate effect of an immense number of vibrations with definite values, they present, under similar conditions, absolutely the same appearance, whereas the eye in observing vibrations rapidly repeated, sees only the average effect. Many observations impossible by the eye are easily obtained by photography, and hence the adaptability of spectrum photography to quantitative analysis.

Some of the applications of the method may be mentioned: (1) the quantitative analysis of small quantities of minerals, such as crystals, a few milligrams in weight; (2) the analysis of globules of metals reduced by the blow-pipe; (3) the determination of the composition of rare coins and antique jewellery, the spark causing no damage to such articles; (4) the estimation of the minute constituents in ores and metallurgical products. Proceeding in the manner which has been already described; a reference to the maps of quantitative spectra will indicate how such analyses are made (figs. 18 and 19).

(20) **The detection of phosphorus in cases of poisoning.** When phosphorus, or a compound capable of reduction, such as ferrous phosphide, phosphorous acid, or a hypophosphite, is introduced into a hydrogen apparatus, the flame shows a magnificent green nucleus, which is brighter the more the flame is cooled. Salet cools the flame by surrounding the jet with a moderately wide tube of glass, with a lateral side tube through which cold air can be blown, the arrangement being similar to a Herapath's gas blow-pipe, air taking the place of gas and hydrogen that of air. With this arrangement a

series of bands can be observed with the spectroscope.

The wave-lengths of the bands are as follows:

Millionths of a millimetre

δ { 609 Weak diffuse.
599 Maximum; de-graded towards the violet.
590 Weak and diffuse. }
584 Weak and diffuse.
Greenish Yellow β { 576
559
522 }
Green α { 547 Weak and de-graded towards the violet.
525 Maximum; de-graded towards the red. }
Green γ { 511 }

Weak bands at 503, 491, 478, 470.

When the flame is not cooled, the order of intensity is no longer α, β, γ, but α, γ, β; and δ is no more than barely visible (G. Salet, 'Traité de Spectroscopie,' p. 177, Paris, 1888).

(21) **The estimation of phosphorus in iron and steel.** Sir J. G. N. Alleyne in 1875 (Journal of the Iron and Steel Institute) devised a method of estimating phosphorus in iron and steel. The metal is submitted to the action of the spark in an atmosphere of hydrogen, this gas being displaced by carbonic acid in measured volumes. No lines of phosphorus are visible when the sparks pass through hydrogen, but in presence of air, or on the gradual admission of carbonic acid the lines shine out, and are brighter the more gas is admitted or the more phosphorus is present. To produce the sparks a coil capable of giving a spark $16\frac{1}{2}$ inches long in air was used; the sparks were condensed by Leyden jars of great capacity, the electrodes being so adjusted that a continuous series of discharges took place between the poles. The spectroscope was fitted with fine flint glass prisms. The tubes in which the electrodes are inclosed are connected with a supply of coal-gas, a gas-holder of hydrogen, and a generator for carbonic acid. The air is displaced by coal-gas; this is displaced by measured volumes of hydrogen, and in turn is removed by carbonic acid. The movement of the hydrogen and carbonic acid into the tube is caused by water flowing out of an aspirator, which is graduated. The stream of water is shut off as soon as two green lines appear, and the quantity of water displaced by carbon dioxide is a measure of the phosphorus present. This is found by reference to a curve derived from actual experiments made with a series of analysed irons and steels. The spectrum is carefully described, but no wave-length measurements are given. The spectrum of phosphorus obtained by a disruptive discharge is composed of the following lines:

6506, 6463, α group { strong 6046, 6035, strong 6025, } β 5498, 5461,
5452, γ 5420, 5341, 5310, 5283, δ, fairly strong,
5248, 4943, ε { 4602 } 'Traité de Spectroscopie.'
{ 4589 } G. Salet, p. 198.

By comparison with the drawing and description of the spectrum, it appears that the lines to be looked for are the pair ε { 4602, 4589 } in the green, a little more refrangible than F. The

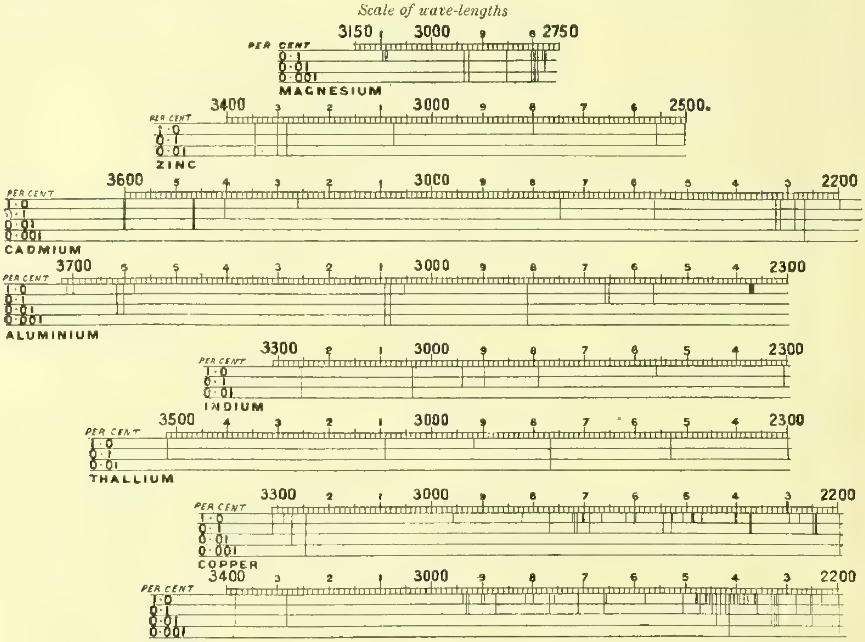


FIG. 18.—QUANTITATIVE SPECTRA.

Maps of metallic spectra photographed from solutions of known strength.

group *a* is that which is described as being 'like a wicket with the middle stump very thin'; it lies in the red.

(22) **The analysis of iron and steel.** Messrs. Parry and Tucker have photographed sparks passed between iron points, and consider the results obtained as of great value, but generally speaking it is necessary, on account of the multitude of iron lines, to separate the iron from the foreign metals. To examine steel thoroughly, dissolve about 7000 grains in *aqua regia*, evaporate to dryness, and heat on a paraffin bath to 250°C. until the acids are expelled. Drench with strong ammonia, and pour into a stoppered bottle; fasten down the stopper, and digest for several hours in a warm place. The ammonia is filtered off and evaporated, first with nitric and then with hydrochloric acid (solution A).

Boil the residue with water, filter and evaporate the liquid (solution W).

Add acetic acid to the residue and boil; nearly neutralise with ammonia and boil again, filter, and evaporate the solution (solution A′).

On proceeding thus, and photographing the spark spectra of the solutions, the following metals were detected in Bessemer steel:

In solution A (ammonia), nickel, cadmium, calcium, manganese, copper.

In solution W (water), calcium, manganese, copper.

In solution A′ (acetic acid), antimony, aluminium, lead, calcium, manganese, copper.

It may be remarked that calcium was not necessarily in the metal, for it is always present in acids and in floating dust. The ultra-violet spectra should be photographed from these solutions.

In photographing condensed sparks from iron points a means is afforded of estimating the amount of carbon and silicon present by the presence of the lines of those elements, and a comparison therewith of a series of standard spectra. Manganese is capable of being so estimated, but for this purpose it is necessary to separate the iron by solution and precipitation.

(23) **Examination of the Bessemer blow.** During the Bessemer 'blow' the appearance of the flame which issues from the mouth of the converter indicates to the eye of a skilled workman the exact moment when the blast should be turned off. By the use of the spectroscope the changes in progress may be ascertained. Roscoe's first observations showed that at a certain phase of its existence the flame emitted a complicated but characteristic series of (*a*) bright lines, (*b*) bright bands, and (*c*) absorption bands. Amongst the lines were recognised those of hydrogen, sodium, lithium, potassium, iron, and nitrogen, with many others. A banded spectrum was observed, which at first was stated to be that of carbon. A further investigation by Marshall Watts showed the most striking groups of bright bands, and several lines are due to manganese dioxide, but not to metallic manganese nor to carbon. In a highly manganiferous pig iron this banded spectrum of manganese dioxide has been observed by Grenier to be so brilliant that in order to look at the flame it was necessary to use neutral-tinted glasses, and brown fumes of manganese dioxide were noticed in profusion during its continuance. Marshall Watts' measurements of the manganese dioxide spectrum are given as follow; the thickened figures are measurements at the bright edges of bands, the others refer to lines: 6234, **6204**, 6185, **6178**, 6080, 6060, 5932, **5909**, 5847, maximum of light here; 5847, 5688, **5644**, **5607**, **5580**, 5433, **5423**, 5395, **5391**, **5359**, degraded towards the red, **5229**, **5192**, **5157**, **5099**, **5018**, **4984**, **4943**, **4904**, **4862**, **4836**, 4832, and **4783**.

When the whole of the manganese has been burnt away, the spectrum suddenly disappears

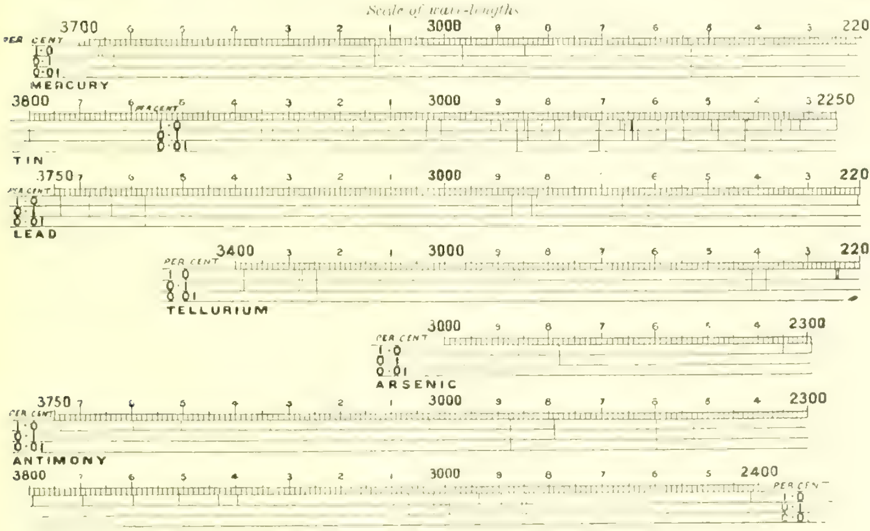


FIG. 19.—QUANTITATIVE SPECTRA.

Maps of metallic spectra photographed from solutions of known strength.

and at this point the combustion of the iron, which is injurious, begins to take place. The reason why the disappearance of the manganese dioxide spectrum coincides with the complete removal of the carbon from the metal is because the atmosphere of the converter, as long as there is carbon to burn, is a reducing atmosphere, being highly charged with carbon monoxide. When this gas has been expelled, and there is no more carbon to burn, the vapour of manganese becomes oxidised, and as soon as the air is in excess, the spectrum of manganese dioxide ceases.

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W. N. H.

SPECULAR IRON ORE *v.* Iron.

SPECULUM METAL. An alloy of 1 equivalent of tin and 4 equivalents of copper and a small quantity of arsenic, used for making the mirrors of reflecting telescopes.

SPEISS *v.* Cobalt.

SPELTER *v.* Zinc.

SPERMACETI is principally obtained from the cachalot or sperm whale, *Physeter macrocephalus*, although it is also procured in smaller quantities from *P. tursio* and *Delphinus edentulus*. It is also to be found in the blubber of *Balænoptera rostrata*, and in the oil of *Delphinus globiceps*. In old works the name is written *sperma ceti*, in the belief that the substance was the spawn of the whale. In 1686 the body of a dead whale which was discovered off the Norfolk coast was found to contain spermaceti, the origin of which was then first ascertained. The Greenland whale fishery had long been carried on before the haunts of the sperm whale were discovered; but we find that between 1775 and 1779 the Americans were taking large quantities of sperm oil, and in 1776 the British Government offered a premium to the ship which should bring home the largest cargo of sperm.

The wax is found in largest quantity in the head of the whale, where it appears as crystals mixed with the fluid oil, nearly a ton of matter being recovered from the cellular tissue contained within the cavity immediately after capture. It exists also in other parts of the body, but does not there solidify until after the melting and cooling out of the fat. The oil, after melting, soon deposits thick scales of spermaceti, and arrives at the factories in a semi-solid condition. The mass there undergoes a series of filtrations and pressings; and finally a little caustic potash is added to the now almost white spermaceti, by which means the last trace of colour is removed. The material is then cast in blocks.

Crude spermaceti forms yellowish transparent plates of a foliated structure, with a rancid, fishy odour. After treatment with potash lye as above described, it is white, semi-transparent, and crystalline, tasteless, odourless, and friable. The product of the right sperm melts at about 45°, and congeals immediately below that point; the spermaceti of the bottle-nose and some others melts at a somewhat higher point. Purified spermaceti, again, after repeated treatment with hot alcohol, has its melting-point further raised, and can be distilled at 360°, without perceptible decomposition or alteration. It is readily soluble in ether, chloroform, and bisulphide of carbon; but is insoluble in water, and very slightly soluble in cold alcohol, benzene, and petroleum.

Spermaceti consists mainly of cetyl palmitate $\left.\begin{matrix}C_{16}H_{31}\cdot\\ C_{16}H_{33}O\end{matrix}\right\}O$. It is difficult to saponify, but, on long boiling with potash, yields cetyl alcohol, the *ethal* of Chevreul. Its specific gravity at 15° is 0·943.

The flame produced by burning spermaceti is large and clear; it is therefore employed in candle-making, but generally with a small admixture of wax from other sources to correct its brittle character. It was formerly prescribed internally for irritation and inflammation of the alimentary canal and of the bronchial membrane; but its employment as a medicament at the present day is confined to ointments and salves. England and the United States supply most of the spermaceti of commerce. A finer variety is prepared by the French in square cakes of about 35 lbs. each. Of this there are two qualities, one dry and pure white, the other more fatty and of yellowish hue. The inferior quality of American spermaceti is grey-yellow, and contains much oil (see Field, Cantor Lectures, 1883; Brannt, 'Animal and Vegetable Fats and Oils').

SPERM OIL *v.* Oils, fixed, and fats.

SPHACELINIC ACID *v.* Ergot of rye.

SPHENE *v.* Calcium; also Titanium.

SPIEGEL EISEN *v.* Iron.

SPINEL. *Magnesium aluminate v.* Aluminium.

SPIRIT OF AMMONIA *v.* Ammonia.

SPIRIT OF HARTSHORN *v.* Ammonia.

SPIRIT OF SALT *v.* Hydrochloric Acid.

SPIRIT OF WINE *v.* Alcohol.

SPIRIT VARNISHES *v.* Varnishes.

SPODUMENE *v.* Lithium.

SPRUCE OCHRE. *Brown ochre v.* Pigments.

SQUILL. (*Scilla; Scille*, Fr.; *Meerzwiebel*, Ger.)

The fleshy bulb of *Urginea Scilla* (Steinheil), a liliaceous plant inhabiting the shores of the Mediterranean (Bentl. a. T. 281). It has been employed in medicine from ancient times as a diuretic and expectorant. The bulb, already dried, is imported into this country mostly by way of Malta. Under the microscope the cells of its modified leaves are seen to be loaded with mucilage, in which numerous needle-shaped or square prismatic crystals of calcium oxalate are suspended (Fl. a. H. 690).

The mucilage of squill contains a *gum*, which is precipitated by basic acetate of lead, an *uncrystallisable sugar* (Fl. a. H.) and *sinistrin* $C_6H_{10}O_5$ (Schmiedeberg, H. 3, 112; B. 12, 704). The sinistrin of Schmiedeberg is probably a distinct substance from the constituent of dahlia root described under the same name by Marquart (A. 10, 91). After removal of the gum from squill mucilage, by treatment with basic acetate of lead, milk of lime is added, when an insoluble calcium compound is formed, from which free sinistrin may be liberated by carbonic acid. It is purified by successive solution in water and precipitation by alcohol. Sinistrin is a white amorphous powder, soluble in water, insoluble in alcohol, is lævorotatory (*cf.* Kühneman, B. 8, 387), and does not reduce Fehling's solution. Diastase is without effect upon it, but by boiling with dilute acid it is converted into lævulose and inactive glucose. The 'scillin' of Riche and Rémont (J. Ph. [5] 2, 291) appears to be nearly related to sinistrin.

By treating an alcoholic extract of squill with tannic acid, a compound is obtained containing the bitter and more active constituent of squill. This has not been satisfactorily isolated, although under the name of *scillitin* or *sculeïn* it has been much investigated. See further Mandet (C. R. 51, 87), Schroff (N. R. P. 14, 241), Righini (R. 63, 87), Tilloy (J. Ph. 12, 635; [3] 23, 406), Vogel (S. 6, 101), Lebourdais (A. Ch. [3] 24, 62), Marais (J. Ph. [3] 30, 130), Landerer (R. 47, 442). A bitter pulverulent compound, *scillaïn*, has, however, been obtained by Jarmersted, which, in its physiological action, resembles digitalin (J. 1879, 914). It is a glucoside, difficultly soluble in water but soluble in alcohol. The names 'scillipicrin,' 'scillotoxin,' and 'scillin' have been applied commercially to condensed pharmaceutical preparations of squill (Merck, Ph. [3] 9, 1038). A. S.

STALAGMOMETER *v.* Fusel oil.

STANNATES. Compounds of stannic oxide with bases, *v.* Tin.

STANNIC ACID *v.* Tin salts and oxides.

STANNO-FLUORIDES *v.* Tin salts and oxides.

STARCH (Lat. *Amylum*; Fr. *Amidon, Fécule*; Ger. *Stärke, Stärkemehl, Farina*).

1. *Occurrence.*—In some form or other starch is one of the most widely-diffused substances in organic nature, occurring more or less abundantly in every plant that has, up to the present time, been examined. It is found in larger quantities in some families of plants than in others, and occurs in different parts in different plants; for instance, it is always found in great abundance in the seeds of all the cereals, as well as of the leguminosæ, in the stems of various species of Sagus and Cycas, in the roots of many plants belonging to the family of Euphorbiaceæ and Zingiboraceæ, and in the tubers of the potato, canna, and cassava.

Starch is also found under varying conditions in different parts of the same plant; for instance, it is found in the green leaves of all plants during the daytime, the proportion varying according to the weather and time of day. It is generally present in greatest quantity towards the evening and least in the morning, whilst during the night the starch almost or completely disappears from the leaves, especially during the summer months. Starch is also found in the pith of trees and shrubs and in the various woody tissues; but its presence in these parts, as in the leaves, is not constant and equal, the same tissues at certain seasons being fully charged with starch and at others almost entirely devoid of it.

2. *Nomenclature.*—In this country the term 'starch' appears to be applied generally to that obtained from all sources, with the name of the substance from which it is prepared usually prefixed to it, such as 'potato starch,' 'wheat starch,' 'rice starch.' In a few instances the affix starch is dropped, as in 'sago,' 'arrowroot,' or the product is known by some name given it in commerce, as 'tapioca,' 'tous-les-mois.'

In France the term 'fecula' (*fécule*) is applied to the starch obtained from roots and tubers, such as potato, manioc, arum; from stems, such as sago; and from fruits and seeds, as horsechestnut, acorns, &c.; whilst the starch obtained from all the cereals is defined as amidon or starch. Most of these products are known in Germany as 'farina.'

Table I.—*Relative proportions of starch per cent. in various plants.*

—	Krocker	O'Sullivan
Wheat . . .	53–56	54–55·5
Barley . . .	38·6–37·9	46·2–46·4
Oats . . .	27·9–36·9	35–38
Rye . . .	45–47	44–46
Maize . . .	66–67	54–58
Rice . . .	—	75–77

Table I. (*continued*).

Buckwheat . .	44	Krocker
Millet . . .	53·7–55·5	"
Haricot beans .	37·7	"
Peas . . .	38·8	"
Lentils . . .	39·6–40	"
Potatoes (air-dried)	16–23	"
Acorns . . .	64·5	Gzubata
Pollen of common pine	7·1	Von Planta
Green bananas .	12·1	Ricciardi
Soja bean under	5·0	Meissl & Böcker
Leaves of caoutchouc tree	5·4	—
Liquorice root .	29·6	Sestini
Nasturtium officinale	2·9	Church
Tubers of yam .	25·2	Moser
Dried pears . .	10·3	Bertram
" apples . .	5·2	"
Parsnips . .	1·0	Corenwinder
Kola nuts . .	33·7	Heckel & Schlagdenhauffen

3. *Physical characteristics.*—To the naked eye pure starch presents the appearance of a white glistening friable powder, having a harsh feel when rubbed between the fingers, perfectly neutral, without taste or smell, is uncrystallisable, and undergoes no change under ordinary atmospheric conditions. Under the microscope it is seen to consist of granules of various forms—in most cases, however, more or less ovoid—and differing widely in size, form, and appearance, dependent on the source from whence they are derived. According to Payen, they may vary in size from ·002 mm. in diameter to ·185 mm. These wide differences are the principal means by which the various kinds of starch may be differentiated one from another as they occur in commerce.

Table II.—*Diameters of the commoner varieties of starch granules.*

Starch from	Millimetre.
Rhizomes of *Canna gigantea* . .	·175
" " *Maranta arundinacea* (arrowroot)	·140
Tubers of potato	·140
Broad beans	·075
Sago	·070
Lentils	·067
Haricot beans	·063
Peas	·050
Wheat	·050
Tubers of *Batata edulis*	·045
Maize	·030
Tapioca (*Jatropha manihot*) . .	·028
Barley	·025
Rice	·022
Millet (*Panicum miliaceum*) . .	·010
Buckwheat	·009
Parsnip	·007
Seeds of beetroot	·004

It must be noted, however, that the size of the starch granules varies very considerably in different plants, being in some immeasurably minute, as in certain species of cactus; in others, as in the potato and tous-les-mois, attaining a comparatively very large size, the several grains being readily visible with a simple lens.

In the same plant—and, indeed, often in the same cell—the size of the starch granules will be found to vary, being chiefly dependent on the relative age of the grains, so that when measures of starch grains from various sources are given they must be taken only to represent an average; but although the dimensions of the starch granules produced by any one species of plant are by no means constant, yet none of them depart very widely from this average, and so by reference to such a standard the starch granules of different plants may readily be differentiated microscopically one from the other by an expert.

4. *Formation of starch in the living plant.* Starch granules in the growing plant are formed in the homogeneous solid substance (protoplasm) of the chlorophyll corpuscles. They are at first visible as mere points, and gradually increase in size, so that eventually they may so completely fill up the space of the chlorophyll corpuscle that this may be represented by a mere covering film, and at last almost entirely disappear. These starch granules are sometimes extremely minute and very numerous, and so closely packed together as to fill the cell cavity, as in the case of rice and oat, whilst in other instances they are of much larger dimensions, so that only a comparatively small number of them are to be found in each cell.

Starch granules only grow and increase in size so long as they are in contact with the protoplasm and are exposed to light at a favourable temperature in the presence of carbonic anhydride. Hence the formation of starch in the leaves of the growing plant must be regarded as a product of assimilation, and may be supposed to take place somewhat in the following manner. It is well known that carbohydrates can be oxidised to aldehydes, and arguing from this Baeyer suggested (Ber. 3, 63) that formaldehyde is the immediate product of assimilation, and by its condensation gives rise to the polymeric substance glucose—thus: $(CH_2O)_6 = C_6H_{12}O_6$, and hence to the anhydride of it, starch. If this be the process which actually occurs in the plant, the function of chlorophyll is simply the decomposition of carbonic anhydride into carbonic oxide and oxygen (Vines, C. J. 33, 375). That such is the case would appear from experiments recently recorded by Bokorny (C. C. 1888, 858; 1891, 120), who finds that algæ (*Spirogyra majuscula*), when placed in a culture solution containing 0·1 p.c. methylal, or 0·1 per cent. of sodium hydroxymethyl sulphonate, and 0·1 p.c. K_2HPO_4, and allowed to remain in air free from carbonic anhydride and exposed to the light, contained, at the end of five days, very considerable quantities of starch, the sodium hydroxymethyl sulphonate being broken up into sodium sulphite and formaldehyde, which by condensation becomes converted into carbohydrate.

As fast as the starch—the raw material of the plant—is formed in the leaves it is withdrawn by the growing plant for various purposes. According to Vines, one portion becomes converted into cellulose to form the walls of the cells in growing organs, this cellulose becoming subsequently converted into lignin or cork, or gum and mucilage. A second portion is devoted to the nutrition of the existing protoplasm, and to a formation of new proteid material by the combination of carbohydrates with derivatives of the nitrogenous compounds (ammonia and nitrates) absorbed by the roots. A third portion probably undergoes decomposition to form the colouring matters, acids, &c., and furnishes, in consequence, energy to the plant, and the remainder of the carbohydrates is stored up in the persisting parts of the plant, either as carbohydrate (starch, inulin, cane sugar, &c.) or as oil and fat.

5. *Structure of starch granules.*—Starch granules, when examined under the microscope with a sufficiently high power, are found to consist of a series of distinctly stratified concentric layers, the outer ones being denser than those nearer the nucleus or hilum, which appears as a dark spot and generally occupies an eccentric position. This is well seen in potato starch. Occasionally two or more nuclei appear in one granule, and concentric layers may be observed surrounding each, as in the case of the haricot bean. These granules consist principally of a substance called 'granulose,' together with small quantities of another substance very closely allied to granulose, and known as starch cellulose. This substance preponderates in the outer layers of the granule, the entire outer coating being in all probability composed of it. This outer layer is the oldest in point of growth; the starch granule, according to Nägeli, increasing in size from without inwards, so that each interior layer is younger and less compact than the one which immediately surrounds it; and since these layers are for the most part of variable thickness they cause the granule to deviate gradually in form from the originally spherical nucleus and assume a more or less ovoid form.

To the presence of this protective coating is to be attributed the fact that starch granules, when intact, are absolutely unacted upon by cold water. Although water is absorbed to a very large extent by the granulose, none of this substance, which is to the highest degree colloidal, is able to diffuse into the surrounding medium.

If, however, the outer layer of the granule be ruptured by attrition, water is rapidly absorbed, the cell contents become swollen to a very great extent, and a small quantity of matter goes into solution. By treating the ruptured starch grains repeatedly with water the whole of the granulose may be removed, whilst the cellulose remains behind in the form of extremely thin layers; treated with a solution of iodine these give a dirty-yellow colour. Granulose, on the other hand, is coloured an intense indigo blue with iodine solution; this reaction, which is most characteristic of all starches, will be referred to again later on.

Granulose may be separated from starch cellulose by allowing a 2 p.c. solution of sulphuric acid to act upon the starch granules for a few weeks, but the easiest way of obtaining it is by acting on starch paste (5–6 grms. per 100 c.c. water) in the cold, with diastase or cold water malt-extract. Limpidity is produced in a few minutes, the liquid is filtered, and the residue, which consists of starch cellulose, is washed well with cold water. Starch cellulose obtained in this way is perfectly insoluble in cold water, or in water heated up to 80°C.; it is not acted upon by diastase in the cold, nor up to 60°C. By boiling with water, however, it is converted to a great extent into soluble starch; a portion of it, however (about one-fifth), resists the repeated action of boiling water, but is readily dissolved in a dilute solution of potash, from which the greater portion of it can be re-precipitated by the addition of acetic acid. If, however, the alkaline solution be heated up to boiling, the whole of the cellulose is slowly converted into soluble starch. Well-washed potato starch contains from 2 to 5 p.c. of cellulose.

Under polarised light starch assumes a most characteristic appearance. When examined under crossed Nicol prisms the field remains dark, but each granule assumes a glistening grey appearance, as if self-luminous, and is marked with a black cross. If, then, the object be slowly rotated in the field of view, the cross will remain fixed with regard to the field, one pair of its arms being parallel to the principal plane of the polariser, and the other parallel to the principal plane of the analyser. If next the object be allowed to remain stationary, and the polariser or analyser be rotated, the cross will rotate with it, but with only half the angular velocity; if, next, a thin plate of selenite be introduced between the polariser and the object, and whilst the Nicols are crossed, most beautiful chromatic effects may be obtained.

6. *Chemical properties.*—Starch is absolutely insoluble in cold water, alcohol, ether, or any other known solvent.

Ordinary air-dried starch usually contains about 18 p.c. of water, which may be entirely driven off by heating for some time in a current of dry air at a temperature of 100–105°C. Under this condition starch appears to be a most highly hygroscopic substance, which rapidly absorbs moisture from the air until it regains its original 18 p.c.; if exposed to a damp atmosphere it is capable of absorbing as much as 35 p.c. of moisture.

7. *Action of heat.*—Freed completely from moisture, starch may be heated to a temperature of 160°C. without undergoing any change; at temperatures higher than this it becomes coloured, and is partly converted into dextrin. If, however, ordinary air-dried starch be heated to 160°C. it quickly undergoes decomposition, becoming converted to a greater or less extent into dextrin and reducing sugars, the action (*v.* DEXTRIN) varying with the particular kind of starch used.

Experiments were made by the writer as to the effects of heat on different varieties of starch. Potato, sago, and rice were heated to 190°C. for two hours, cooled down, dissolved in cold water, and the specific rotatory powers of the solutions taken.

The potato- and sago- starch are entirely decomposed under these conditions, and their solutions showed a specific rotatory power of $\alpha_D = 154{\cdot}3$ for potato, and $\alpha_D = 193{\cdot}3$ for sago; the rice-starch appears to offer great resistance to the action of heat, being only partially decomposed at the above temperature.

According to Schubert (M. 1884, 472), the starch granule, under the influence of high temperature, is altered in such a manner that those layers which are rich in granulose are at once converted into soluble starch and dextrin, while the principal portion of the layers rich in cellulose only undergo this transformation after a time. When starch which has been subjected to a high temperature is treated with cold water, the soluble starch, dextrin, and other products of decomposition go into solution, and an organised residuum is left, which resembles the form and structure of the original granule, and contains small quantities of unchanged granulose.

By dry distillation starch yields carbonic anhydride, gaseous hydrocarbons, water, acetic acid, and empyreumatic oil, and leaves a porous cinder.

On distilling dry starch with lime in the proportion of 1 to 4 it yields acetone, mesityl oxide, a series of ketones, and various condensation products of acetone (Horvat, C. C. 1887, 38).

By distillation with manganese dioxide and dilute sulphuric acid it yields carbonic anhydride, aqueous formic acid, and furfurol.

In the open fire it softens, swells up, evolves choking vapours, and at last burns with a bright flame.

Distilled with hydrochloric acid and manganese peroxide, it yields, among other products, trichlorinated acetic aldehyde and pentachlorinated propionic aldehyde.

8. *Action of hot water.*—When starch is brought into contact with hot water the contents of the granules, owing to a large absorption of water, swell up enormously; and, at a temperature varying according to the variety of starch, ultimately rupture the outer layer, forming a viscous liquid which is known as 'starch paste.'

The different varieties of starch gelatinise with hot water at very different temperatures, as is seen in the following table recently published by Lintner (Brauer und Malzer Kalendar, 1889), which gives the temperatures of complete gelatinisation for the commoner varieties of starch:

TABLE III.

Starch from	Temperature at which complete gelatinisation takes place
Potato	65°C.
Maize	75°C.
Barley	80°C.
Wheat	80°C.
Rye	80°C.
Rice	80°C.
Kilned malt	80°C.
Green malt	85°C.
Oat	85°C.

This table gives the temperatures at which the various starches gelatinise completely in the pure state. In the crude condition a much higher temperature is necessary.

Under the action of boiling water the starch granules do not all swell up and burst at once—the younger ones being attacked first, the older last. This progressive action of heat can be very well observed when potato starch has been suspended in 12 to 15 times its weight of water, and gradually heated on the water-bath; hardly any change is apparent up to 55°C., at 57°C. the younger granules begin to show signs of rupture, and as the temperature rises this process of swelling and bursting of the contents through the outer wall of the granule goes on increasing, the earliest-formed granules being the last to give way, until, at a temperature between 65–70°C., a thick viscous liquid, of uniform consistency, is observed.

According to Bruckner (M. 4, 889), starch-paste and granulose are identical, and no sharp distinction can be drawn between swollen starch granules and starch-paste; thus at 46°C. potato-starch swells distinctly, at 59° it begins to lose its form, and at 62·5° it is converted into a paste and shows no trace of its original form.

On cooling, starch paste contracts and becomes, when very thick, a firm solid mass, which, after standing a short time, cracks; its maximum contraction is reached at the freezing-point, when a separation of the water and starch takes place to a certain extent. Upon raising the temperature, the water which had been frozen out does not again combine with the starch, and may be drained away, whilst the consolidated starch paste remains as a felty mass which, when dry, has the appearance of mother-of-pearl (Payen).

Wide differences in the viscosity of this paste are observed, depending not only upon the variety of starch employed, but also upon the treatment to which the starch is subjected during the processes of purification and drying.

According to Brown and Heron (C. J. 35, 596), starch which has been treated with dilute potash and acid in the process of purification produces a paste of less viscosity than the same starch which has not been so treated; they also find that immense variations in the consistency of the resulting paste are produced by slightly altering the manner of drying. Thus starch which has been dried slowly and at a low temperature yields a more viscous solution than if dried quickly at a higher temperature, as is seen from the following experiments:—

No. I. Dried at 50°C. whilst very moist, and afterwards at 100°C. for twenty-four hours.

No. II. Dried whilst very moist under the air-pump at ordinary temperature, and afterwards in the air-bath at 100°C. for twenty-four hours.

No. III. Dried under the air-pump, and finished at a temperature never exceeding 30°C.

Table IV.—*Relative viscosity of the paste made with the above samples, No. I. being taken as unity:*

No. I.	1·000
No. II.	2·306
No. III.	3·288

In these experiments the paste was made in each case with three grms. of starch per 100 c.c. of water, but since the samples did not all contain quite the same amount of moisture the results are corrected for equal weights of dry starch. The relative viscosity of the solutions was measured by the weight required to sink in them a disc of very thin glass $\frac{5}{8}$ of an inch in diameter. From a manufacturing point of view these experiments appear to the writer to possess a considerable amount of importance, and would be well worth carrying out on the large scale, seeing that the technical value of a starch in certain industries depends entirely upon the viscosity produced by it when acted upon by boiling water.

Potato starch is used in large quantities for the sizing and stiffening of yarn and cloth, so that it is of importance to the manufacturer to obtain that sample of starch which will make the stiffest cloth and which has the greatest tenacity. In order to determine this, the following method has been recommended by Whewell (C. N. 39, 97):—28 grains of the sample of starch the viscosity of which is to be determined are weighed out into a two-ounce evaporating dish, and 26 c.c. of distilled water added, and boiled, with constant stirring for three minutes. The resulting starch paste is then poured into a conical-shaped test-glass of one-ounce capacity. The glass is shaken slightly to make the surface of the jelly level, and then allowed to cool for exactly two hours; in a similar way 18, 20, 22, 24, and 26 grains of starch are gelatinised and poured into exactly similar test-glasses, all of which are labelled respectively 18, 20, 22, 24, and 26. At the end of this time a 100-grain weight ($\frac{13}{20}$ of an inch in diameter) is placed on the surface of the jelly. If it is supported for more than five minutes, it is placed successively on each of the others until it sinks. By this means the viscosity is obtained to within 1 grain. The intermediate number will then be found to support the weight for exactly the right time. The number of grains required is termed the viscosity. Thus if the viscosity of one sample is 18 and the other 28, it means that it requires 28 lbs. of one sample to give the same stiffness as 18 lbs. of the other.

As has already been stated, starch-paste is composed of granulose, which very probably exists in a state of true solution, forming an intensely viscous liquid, and starch cellulose, which remains insoluble. The specific gravity of starch-paste, as determined by Brown and Heron, is 1·66 at 15·5°C. It is one of the most perfect colloids known, and, since its solution-molecule is extremely large, its passage through the fine pores of filter-paper is very difficult. It rotates a polarised ray of light strongly to the right, but owing to the want of transparency in the liquid the determination of its specific rotatory power is exceedingly difficult, it being impossible to obtain good observations with solutions of even very pure starch containing more than 1 grm. of substance per 100 c.c. The mean of Brown and Heron's observations from solutions of this strength give $\alpha_j = 208°$, but it is possible that this number is too high, owing probably to the presence of a small portion of soluble starch, which evidently possesses a higher rotation, for the above authorities state that if a dilute solution of starch-paste (1 grm. per 100 c.c.) be boiled for thirty minutes the liquid becomes much more transparent, and at the same time an increase in the rotation is observed.

9. *Soluble starch.* Under certain circumstances starch undergoes a peculiar modification, by which it is rendered completely soluble in water, from which it can be precipitated as a brilliant white flocculent substance by alcohol, or if the solution be somewhat concentrated and allowed to stand some time, a white granular precipitate slowly separates out. But no matter how slowly it may be precipitated from its solution, it is always found under microscopic observation to be made up of minute particles, entirely without structure and without action on polarised light. Although but sparingly soluble in cold water (not more than 2 or 3 grms. per 100 c.c. ever going into solution), it readily dissolves in water at 60–70°C., and separates out again on cooling as a white flocculent amorphous precipitate. To this substance has been given the name of 'soluble starch.'

When starch-paste is largely diluted with water and boiled for some considerable time, a portion of it goes into solution, and may be easily filtered off. A similar reaction may be brought about more rapidly if starch with about ten times its weight of water be heated under pressure up to 130–150°C. (Stumpf, B. C. 1880, 457). Under these conditions, the greater portion of the starch is rendered soluble.

The same effect may be brought about by treating potato starch with a 5–10 p.c. solution of hydrochloric acid for seven to ten days (Lintner, J. pr. 34, 378, 1886); the starch granules are then washed until free from acid, and, on treating with boiling water, dissolve up completely without the production of the usual viscid paste. This extraordinary change in the properties of the granules is not accompanied by the slightest change of structure, and the altered granules have the same appearance under the microscope and the same influence on polarised light as the unaltered starch.

Soluble starch may be prepared, according to O'Sullivan, as follows: Starch-paste is acted on with the least possible quantity of the cold water extract of malt, previously heated to 75°C. for thirty minutes, or with diastase solution, or with dilute sulphuric acid (sp.gr. 1120) at 75°C., and further action stopped as soon as ever limpidity is produced by raising the liquid quickly to the boiling-point if diastase or malt extract be employed, or by adding barium carbonate if sulphuric acid has been used, until neutrality is produced. The liquid is then filtered bright and evaporated until a slight skin begins to form on the surface; when the soluble starch falls out on cooling as a brilliant white precipitate. This is allowed to rest for a few days, and then treated with cold water, with which it is washed well upon a filter. It is purified by dissolving it in as small a quantity of boiling water as possible, and again filtering, if necessary using a hot-water funnel. On cooling, the soluble starch separates from the filtrate as before.

Perhaps the readiest way of preparing soluble starch is that recommended by Zulkowski (C. C. 1888, 1060), who finds that starch dissolves in hot glycerin and is converted into the soluble modification; this, in turn, if the action be continued, becoming transformed into erythrodextrin and achroodextrin, with the production at the same time of reducing sugars. 60 grms. of dry potato-starch are heated for half an hour with 1 kilogramme of glycerin at a temperature of 190°C., then cooled down to 120°C., and the soluble starch precipitated by the addition of two or three times its volume of strong alcohol. If necessary, the precipitate may be further purified by dissolving again in the smallest possible quantity of boiling water, and reprecipitating therefrom with 90 p.c. alcohol.

Pure soluble starch prepared by any of these methods when in solution rotates a polarised ray of light strongly to the right. Its specific rotatory power is for $[\alpha]_j = 222{\cdot}0°$, $[\alpha]_D = 200{\cdot}4°$, or for 3·86 divisor $[\alpha]_j = 216{\cdot}0°$, $[\alpha]_D = 195{\cdot}0°$ (*v. Saccharimetry*, art. SUGAR). It has no action whatever on Fehling's solution, and, like starch-paste, its solution is coloured an intense blue with iodine.

10. *Action of alkalis.* When a moderately-strong solution of potassium or sodium hydroxide is added to starch paste, the previously opalescent liquid is rendered perfectly transparent without any alteration taking place in its viscosity. This increase in transparency is due to the solution of the suspended starch cellulose by the alkali. The specific rotatory power is at the same time considerably lowered, but resumes its original value if the alkali be neutralised by acetic acid. These facts point to the production of a definite compound of starch with potash or soda. An interesting feature in this reaction is that, after acidification, the solution remains transparent, and possesses all or nearly all the viscosity of the original starch-paste (Pfeiffer and Tollens, A. 1882, 285; Brown and Heron, C. J. 35, 596).

When starch is treated with an alkaline solution the granules swell up and form an exceedingly tough viscous mass, which readily dissolves in water, forming a solution in no point differing from that produced by the action of alkali on starch-paste.

Symons (Ph. [3] 13, 237) has investigated the process of swelling of starch granules under the action of heat at different temperatures, and of alkaline solutions of varying strengths, and concludes that the process of swelling through the action of these widely-differing agents is one and the same, and, as a result of his experiments, proposes a method whereby the several varieties of starch may be detected by their behaviour with dilute alkaline solutions of definite strength.

The most suitable are solutions of caustic soda of 0·5–1·5 p.c. 0·1 grm. of the starch is repeatedly stirred up with 1 c.c. of the particular soda solution, and, after ten minutes, examined under the microscope.

Ammonia solution, either dilute or concentrated, has no action whatever on starch or on starch-paste.

If a trace of starch be added to a solution of a salt of ammonia, and then a solution of sodium hydroxide drop by drop, the starch remains unchanged until the whole of the ammonia salt has been decomposed; but the least excess of soda causes immediately an expansion of the starch granules.

The following tables give the results of Symons' experiments for various starches:

TABLE V.—*Action of heat on starch granules.*

Variety of starch	Order of relative size of granules	Few granules swollen at	Majority of granules swollen at	All granules swollen at
		°C.	°C.	°C.
Potato . . .	2	55	60	65
Cassava . .	7	58	63	68
Natal . . .	4	58	65	70
Wheat . . .	5	60	65	70
Tous-les-mois	1	65	68	72
Bermuda . .	4	62	69	73
Sago . . .	3	64	68	74
Maize . . .	6	65	70	77
Oat	8	65	70	77
St. Vincent .	4	66	73	77
Rice . . .	9	70	75	80

TABLE VI.—*Action of dilute NaHO on starch granules.*

Variety of starch	Order of relative size of granules	Few granules swollen with	Majority of granules swollen with	All granules swollen with
		p.c. NaHO	p.c. NaHO	p.c. NaHO
Potato . . .	2	0·6	0·7	0·8
Oat	8	0·6	0·8	1·0
Natal . . .	4	0·7	0·8	1·0
Tous-les-mois	1	0·7	0·9	1·0
Wheat . . .	5	0·7	0·9	1·0
Bermuda . .	4	0·8	0·9	1·1
Sago . . .	3	0·8	0·9	1·1
Maize . . .	6	0·8	1·0	1·1
Cassava . .	7	0·8	1·0	1·1
St. Vincent .	4	0·9	1·0	1·2
Rice . . .	9	1·0	1·0	1·3

Starch exhibits a peculiar reaction with ammoniacal copper solution. Dry starch readily absorbs cupric oxide from ammonio-cupric oxide solution, and decolourises the liquid, the action being more rapid if the starch has previously been slightly moistened. Starch paste acts in a similar manner. A deep-blue compound is formed, from which water, and even dilute ammonia, remove only traces of copper. Repeated washing, however, with strong ammonia eventually removes every trace of copper (Guignet, C. R. 109, 528).

Dilute hydrochloric acid immediately decomposes this compound, forming chloride of copper, which may be readily removed by washing with water, leaving the starch granules intact.

After prolonged digestion with strong ammonia in the cold, the granules swell up and become converted into the soluble modification.

On heating the compound of cupric oxide and starch with water at 80°C. the starch gelatinises, forming with the cupric oxide a beautiful blue viscous liquid.

Starch possesses the property of combining with other bases than sodium and potassium. If to the transparent colourless jelly formed by acting on starch with sodium hydrate, a 7 p.c. aqueous solution of calcium chloride be added, double decomposition takes place, and a thick, white, insoluble mass is formed, which is a compound of starch with calcium. A series of compounds of starch with other bases may similarly be formed, in which the starch cannot be detected by means of iodine. The starch in such compounds is, however, immediately set free by acids (Payen).

Starch is completely precipitated from a dilute aqueous solution by a solution of lime in sugar-syrup. The composition of the precipitate varies according to the quantity of lime added. With baryta and strontia water similar compounds are formed (C. J. Lintner, Zeit. angew. Chem. 1888, 232).

11. *Action of acids.* A swelling of the starch granules, similar to that occasioned by sodium or potassium hydrate, is produced immediately by all mineral acids, and by some organic acids, tartaric and citric acids, after being in contact for some time. No swelling is produced by acetic or oxalic acids, no matter how concentrated their solutions may be.

When air-dried starch is triturated with concentrated sulphuric acid considerable heat is evolved, and, after a short time, complete carbonisation takes place. If, however, the starch be previously freed completely from moisture, on addition of the acid the granules swell up and form certain mucilaginous compounds of the general formula $C_{6n}H_{10m}O_{5n-x}(SO_4)_x$, which are soluble in water, and rotate a ray of polarised light strongly to the right. When boiled with alcohol they lose all the sulphuric acid, leaving a modified form of starch. Upon neutralising the aqueous solution with bases, uncrystallisable salts are formed (Hönig and Schubert, M. 6, 768).

When diluted sulphuric acid 1 : 2 to 1 : 4 is added to air-dried starch, a swelling up of the granules takes place, and the mass becomes thick and viscous. On standing some hours the viscosity disappears, the iodine reaction showing the presence of soluble starch only; but on standing for some days this becomes gradually hydrated to maltose, and finally to dextrose.

Nitric acid yields with starch various products, depending on the strength of the acid, temperature, and duration of the action.

When starch is boiled for some time with moderately concentrated nitric acid (sp.gr. 1·200) it is completely converted into oxalic acid. Cold concentrated nitric acid (sp.gr. 1·520) added to starch causes the granules to swell up, first into a viscous mass, which after a short interval becomes quite limpid; if now water be added to this solution, according to Braconnot (A. 7, 245), a white powder is precipitated which when dry explodes upon being struck. This substance has been termed xyloïdin, and has the same composition as the corresponding compound of cellulose.

If, however, the solution of starch in nitric acid be allowed to stand, water precipitates less and less of xyloïdin, and at last none, whilst a substance resembling saccharic acid remains in solution (Pelouze, C. R. 7, 713).

Strong hydrochloric acid added to dry starch causes the granules to swell up, and in a very short time to become a thick, semi-translucent, viscous mass. If to this a large quantity of cold water be added, a milky fluid results, which consists entirely of the soluble modification. If, however, the swollen mass be allowed to remain for a few days, the soluble starch will be found to have entirely disappeared, whilst at the same time the viscous mass becomes perfectly limpid, and separates into two layers, the lower one consisting of the products of decomposition of the granulose—namely, achroodextrin, maltose, and dextrose—whilst the upper layer consists exclusively of starch cellulose.

As a matter of fact, very little work appears to have been done with respect to the action of mineral and organic acids on raw starch; and further investigation in this branch of the subject is much to be desired.

If, however, the action of very dilute (1-2 p.c.) mineral acids, such as sulphuric or hydrochloric, upon ungelatinised starch in the cold be allowed to continue for some considerable time (two months or more), the granules gradually become disintegrated, a portion becoming converted into dextrose and going into solution, whilst the residual substance retains little or nothing of the original form of the starch granule. Concurrently with these changes, the iodine reaction undergoes considerable modification, the original deep-blue colour gradually giving place to purple, and this, through reddish-purple and reddish-brown, to a pale yellowish-red, which is not further modified, even if the starch remain in contact with the acid for some years. This residual substance, after being washed with cold water until free from acid, is completely soluble in hot water, from which it may be precipitated by alcohol in the form of a brilliant white powder, which is highly crystalline in appearance when the precipitation has taken place slowly. This, under the microscope, is seen to consist of sphæro-crystals made up of thin needles or plates arranged radially, and so closely resembling the sphærocrystals of inulin that the two substances cannot be distinguished by microscopical examination alone. This substance has been termed amylodextrin by Nägeli. It gives an intense reddish-brown colouration with iodine (Brown and Morris, C. J. 55, 449).

The further action of acids on starch differs very considerably according to the degree of concentration, temperature, and pressure.

When starch is heated to boiling with very dilute acids (2 p.c.), little or no formation of paste takes place, the starch being rapidly converted first into soluble starch, then into dextrin and maltose, and, if the action be sufficiently prolonged, finally into dextrose. If this action be stopped at various stages by neutralising the acid with calcium or barium hydrate, and the filtrates examined at a very early period, the liquid will be found to consist almost entirely of a solution of soluble starch. Later on, this disappears, giving rise to dextrin and maltose; and, according to Brown, Morris, and Moritz (Eng. Pat. 19,003, 1889), to a series of intermediate bodies known as maltodextrins. A little later, dextrose makes its appearance, and this continues to increase at the expense of the maltose already formed, the dextrins and maltodextrins being successively hydrated to this body, until finally dextrose only is found in solution. If, however, the action be carried to this extreme point, the dextrose in its turn is acted upon by the acid, giving rise to condensation products, caramel, and other humous substances (Valentin, Jour. Soc. Arts, 24, 404; Scheibler and Mittelmeier, B. 23, 3060).

At higher temperatures than 100°C., or under pressure, the above changes take place very rapidly. The following table gives some idea of these relative changes:—

TABLE VII.—*Action of sulphuric acid (dilute) on starch at different temperatures.*

Time	Colour of solution	Iodine reaction	$[\alpha]_{D3\cdot86}$	$K_{3\cdot86}$
Series A.—2 p.c. acid. Temperature, 150°C.				
30 secs.	None	Full brown, trace of starch	142·2	42·3
2 mins.	None	Brown	87·2	62·2
5 ,,	Slight	None	61·7	89·1
10 ,,	Much	—	56·8	81·2
30 ,,	—	—	54·3	71·6
Series A.—2 p.c. acid. Temperature, 125°C.				
2 mins.	None	Blue	All soluble starch	
5 ,,	None	Brownish-violet	163·0	29·2
10 ,,	None	Brown	128·6	55·4
Series B.—1 p.c. acid. Temperature, 150°C.				
30 mins.	None	Full brown	152·6	32·2
3 ,,	None	None	83·5	59·6
5 ,,	Light-straw	—	61·1	78·7
Series B.—1 p.c. acid. Temperature, 125°C.				
10 mins.	None	—	153·4	34·3
20 ,,	None	—	118·5	55·6
30 ,,	None	—	97·2	69·7

Table VIII.—*Action of various acids on starch at* 150° C.

Acid	Time	$[\alpha]_{j\,3\cdot86}$	$K_{3\cdot86}$
·25 p.c. Sulphuric .	10 mins.	138·9	38·2
·25 p.c. Hydrochloric .	10 ,,	60·6	84·1
2 p.c. Phosphoric .	10 ,,	117·8	55·1
1 p.c. Tartaric . .	20 ,,	170·3	24·6
1 p.c. Oxalic . .	10 ,,	94·4	76·5
1 p.c. Acetic . .	30 ,,	No action	

12. *Action of chlorine, bromine and iodine.* Chlorine gas has no action on starch granules either in the dry state or when moistened with water, but when passed through thin starch paste for some hours the viscosity disappears, the greater portion of the granulose becoming converted into soluble starch and erythrodextrin; this action takes place slowly in the cold, but quickly at a high temperature.

Bromine colours starch granules yellow, but does not seem to form any definite compound, as the yellow colour disappears on repeatedly washing the granules with water.

Very little action is produced on starch paste by bromine in the cold, but if heated on the water-bath for some time the starch paste is liquefied and converted into the soluble form.

The most characteristic reaction for starch, wherever it occurs, is the production of a deep-blue colouration with a solution of iodine. This colouration is imparted by the iodine to the granulose in the intact starch granules as well as when in the condition of starch paste and of soluble starch. This iodine reaction was discovered as far back as the year 1813 by Stromeyer, and has been the subject of much investigation since then.

When an aqueous solution of iodine is added to starch paste a most intense deep indigo-blue colouration is produced. This blue colouration—which is a most characteristic test for starch, not being produced by any other known body—is due to the formation of a definite chemical compound, or probably more than one compound, of iodine and starch granulose, and is provisionally termed iodide of starch.

It is best prepared by adding an excess of iodine to a thin solution of starch; iodide of starch then separates out as a blackish violet powder, which, when washed, to free it from excess of iodine, and dried, presents the appearance of a black shining mass exhibiting a coppery lustre. Perfectly dry iodide of starch may be heated for several days to a temperature of 100°C. without undergoing decomposition; it may, therefore, be regarded as a very stable body. In the presence of moisture, however, it is decomposed, with, if heated in closed vessels, formation of hydriodic acid, whilst, if it be heated in open vessels, part of the iodine is volatilised, the remainder being converted into hydriodic acid.

Iodide of starch is also formed when dry starch and an alcoholic solution of iodine are triturated in a mortar, provided the alcohol contains water; with absolute alcohol a brown colour is produced, which, on addition of water, changes to blue. Iodide of starch is not formed when iodine vapour is passed over dry starch, but by using moist starch the iodide is formed; from this it would appear that water is necessary to the formation of iodide of starch (Stocks, C. N. 56, 212; 57, 183).

It is also formed by the action on a mixture of potassium iodide and starch paste of such reagents as liberate iodine from its compounds. Such are chlorine, bromine, nitric acid, strong sulphuric acid, ferric chloride, potassium permanganate, &c., all of which cause the characteristic blue colour to appear. The blue colour of iodide of starch is destroyed in presence of excess of chlorine or bromine, owing to the formation of chloride or bromide of iodine.

Starch granules have a greater attraction for iodine than unorganised starch. Hence a cold clear solution prepared from crushed starch granules, and coloured blue by iodine, is completely decolourised by adding whole starch granules; similarly starch granules attract iodine more energetically than dextrin (Bruckner, M. 4, 889–912).

Iodide of starch is soluble only in a large quantity of water, but as ordinarily prepared from starch paste it is an opaque mass, and when examined under the microscope presents the appearance of blue flocculent masses of the iodide floating about in the liquid portion. In this state the blue colour is destroyed by heat (Stocks, C. N. 56, 212; Tomlinson, P. M. [5] 20, 168), but the change is gradual, the liquid becoming first greenish, then yellowish, and finally colourless, and if at this point it be allowed to cool the blue colour does not again appear, although it does so if the heating be discontinued at the yellowish stage and the liquid be allowed to cool; this decolourisation is due to the formation of hydriodic acid.

When iodide of starch does not contain an excess of iodine, alcohol, ether, carbon bisulphide, or benzene fail to extract any iodine from it; if, however, the iodide be heated with alcohol it becomes rapidly decolourised, ethyl iodide being formed at the same time.

13. *Action of other reagents.* Potassium permanganate exercises a powerful reducing action on starch, but instead of dextrin a series of gummy acids are produced, which reduce Fehling's solution only to a very slight extent. Powdered potassium permanganate is added to a 2½ p.c. starch-paste; much carbonic acid is evolved, and manganic dioxide precipitated. The solution is filtered, neutralised with acetic acid, concentrated lead acetate added, the resulting precipitate washed with hot water, decomposed with hydrogen sulphide, the solution concentrated and poured into absolute alcohol, when a curdy precipitate is formed. This is washed with absolute alcohol and ether, and dried *in vacuo* over sulphuric acid. The bodies formed possess dextrorotatory powers, which vary according to the quantity of permanganate employed, and give reactions with iodine from reddish-violet, through reddish-brown, to brown. The elementary analysis of a product which was not coloured by iodine agreed with the formula $C_{12}H_{22}O_{11},C_{12}H_{20}O_{10}$ (Lintner, Zeit. ang. Chem. 1890, 546).

Tannic acid gives a flocculent leathery precipitate with starch paste, as well as with soluble starch, which is soluble in boiling water but is reprecipitated on cooling.

14. *Action of enzymes.* It has long been known that certain enzymes—or, as they are more generally termed, the soluble or unorganised ferments—exert a most powerful action on gelatinised starch, as well as on some of the varieties of starch in the raw state. Of these, the most active are the diastase of malted barley, the saliva, and the pancreatic juice.

If the action of a solution of any one of these ferments on starch-paste be watched, the very first effect produced will be complete liquefaction of the paste, and the production, in an incredibly short space of time, of a perfectly limpid liquid. At this instant, if the liquid be tested with iodine, a reaction for pure soluble starch may be observed; immediately following this comes the saccharification of the soluble starch. The blue colour produced by iodine disappears, giving place to a reddish-brown colour, indicating the presence of erythrodextrin, which in turn becomes transformed into achroodextrin, when iodine ceases to impart any longer a colour to the liquid. At the same time, concurrently with the disappearing of the starch, the proportion of sugar goes on increasing, and continues to do so for a considerable time after the iodine has ceased to show any reaction.

Although starch in some form or other enters so largely into the food of man and beast, it was not until early in the present century that it received any attention from the hands of chemists. Since that time, however, much attention has been bestowed upon the changes which it undergoes under the influence of heat, acids, and certain vegetable and animal extracts, and much valuable information has resulted therefrom.

Considering the very important part which starch plays in several industrial processes on the one hand, and how a careful study of its various transformations serves to throw very considerable light upon many questions connected with vegetable, as well as animal, physiology, it will, perhaps, not be altogether out of place to give, as briefly as possible, a history of the transformations of starch from the earliest up to the present time.

15. *History of starch transformations.* In the year 1811 Vauquelin discovered that when starch is heated to a high temperature it is converted into a substance completely soluble in water, and which resembles gum arabic in many of its physical properties. In the following year Vogel found that a similar substance is formed when starch is acted upon by hot dilute acid. About the same time, Kirchoff discovered that starch, when boiled with dilute sulphuric acid, yields a crystallisable sugar; and two years later, in 1814, the same chemist observed that a similar transformation is brought about by the action of the vegetable albumin of grain, and also that the action of this substance is much intensified by subjecting the grain to the malting process.

The gummy substance produced from starch by the action of dilute acid was first carefully examined in 1833 by Biot and Persoz, who gave to it the name of *dextrin*, from the property which it possesses of rotating a polarised ray of light strongly to the right.

Biot and Persoz did not look upon dextrin as a decomposition product of starch, but considered it rather as consisting of the contents of the starch granules freed from their outer coating by the action of the acid. Payen and Persoz—sharing the same view as to the formation of dextrin from starch by the action of an infusion of malted grain, and which they attributed to the presence of a particular transforming agent—named it *diastase*, from its supposed property of separating the interior of the starch granules from their outer envelope. They were the first chemists who prepared dextrin from starch by the action of diastase, and describe it as a substance soluble in cold water and in weak alcohol, and as not coloured by iodine. A few years later Payen stated that the specific rotatory power of his dextrin was equal to that of starch, and that its elementary composition was indicated by the formula $C_6H_{10}O_5$.

He also came to the conclusion that the dextrins produced by the action of dilute sulphuric acid, diastase, and heat respectively were simply physical modifications of one and the same substance.

Up to the year 1860, dextrin was considered as occupying an intermediate position between starch and sugar, the starch being first converted into dextrin, and this, by subsequent hydration, into sugar. But at this period, Musculus brought forward evidence to prove most conclusively that dextrin and sugar are not successively formed products, but are produced simultaneously by a splitting up of the starch molecule. This theory, which met with strong opposition at first, is now generally admitted to be in the main correct.

The dextrin described more in detail by Musculus in 1865 was a body not coloured by iodine, and did not reduce Fehling's solution. It now began to be recognised amongst chemists that there are at least two dextrins derivable from starch—the one coloured red by iodine, and the other giving no colouration with that reagent. These were described by Griessmayer in 1871 as dextrin I. and dextrin II., and in the following year O'Sullivan distinguished them as α and β dextrin. These are now more generally referred to as erythrodextrin and achroodextrin respectively, names first proposed by Brücke in 1872 as indicative of their behaviour with iodine.

In a series of most interesting and important researches extending from 1872 to 1876 (C. J. 25, 579; 29, 479; 30, 125), O'Sullivan proved most satisfactorily that the sugar produced by the action of diastase or acid on starch is not, as had up to this time been generally supposed, dextrose, but is a sugar of the saccharose type, having a considerably higher specific rotatory power than dextrose, and a much less reducing action upon Fehling's solution.

This body had been previously isolated, as far back as the year 1819, by De Saussure, who, however, merely described its crystalline appearance. It was prepared in 1847 by Dubrunfaut, who, from its optical properties, recognised it as a distinct sugar and named it *maltose*. His observations, however, obtained but little notice at the time of their publication, and appear to have been entirely forgotten until the re-discovery of maltose by O'Sullivan in 1872 (C. J. 25, 579). This investigator also gave the results of his examination of the dextrins prepared by the action of diastase and of acid upon starch. These results led him to the conclusion that the dextrins from both sources possess the same specific rotatory power of $[\alpha]_j = +213°$, and have an elementary composition corresponding to the formula $C_6H_{10}O_5$, and although he did not succeed in obtaining any of the dextrins absolutely free from a reducing action on Fehling's solution, yet he adduced good evidence to show that in a state of purity they would possess no reducing action. Both of these dextrins are slowly converted into maltose by the action of diastase.

In 1875 Bondonneau, apparently unaware of the previous work of O'Sullivan, described three dextrins, which he denotes as α, β, and γ dextrins respectively. The first of these corresponds to O'Sullivan's α dextrin and Brücke's erythrodextrin, whilst β dextrin appears to be an achroodextrin. Both of them possess a much lower specific rotatory power than O'Sullivan's, doubtless owing to not being as completely purified. There can now be no doubt that his γ dextrin was nothing more or less than maltose, and as Bondonneau regarded the reducing sugar formed throughout to be dextrose, it is easy to understand that he should fall into such an error with regard to his γ dextrin.

The properties of dextrin and maltose having been thus definitely established, and it having been shown conclusively that these two substances were the only products obtained by the action of diastase upon starch paste under ordinary conditions, the attention of investigators was turned to the influence of time and temperature upon the reaction by which these substances are produced, so that in the history of starch transformation a new field of research was opened up in 1876 by O'Sullivan (C. J. 30, 125). According to this investigator, starch granules which are intact are unacted upon by diastase or the cold water extract of malt; gelatinised starch, however, either in the cold or at temperatures up to 72°C. is readily transformed. He also established the fact that the transformation of starch into dextrin and maltose is not a gradual act of hydration, the dextrin appearing first and the maltose afterwards, but that the two bodies are formed simultaneously, and in certain proportions according to the conditions under which the starch molecule splits up. On this assumption, the splitting up of the starch molecule by diastase takes place according to certain definite equations, the relative proportion of the decomposition products depending upon the temperature at which the transformation takes place, so that, starting with soluble starch, it is possible to obtain a series of equations, each succeeding one containing a molecule less of dextrin and a molecule more of maltose than the one immediately preceding it until we arrive at the final equation. According to O'Sullivan, the following reactions take place :—(*a*) When starch is acted on by malt extract at any temperature below 63°C., if the solution be immediately (five to ten minutes) cooled and filtered, the product invariably contains maltose and dextrin in proportions closely agreeing with 67·85 per cent. of the former and 32·15 per cent. of the latter; $K = 44·1, [\alpha]_j = 170·6°$, and this reaction is represented by O'Sullivan's equation A.

$$\underset{\text{Starch}}{(C_{12}H_{20}O_{10})_6} + 4H_2O = \underset{\text{Maltose}}{(C_{12}H_{22}O_{11})_4} + \underset{\text{Dextrin}}{(C_{12}H_{20}O_{10})_2}.$$

(*b*) When starch is acted on by malt extract at any temperature between 64°C. and 68-70°C., if the solution be immediately cooled and filtered the product invariably contains maltose and dextrin in proportions agreeing closely with 34·54 per cent. of the former and 65·46 per cent. of the latter; $K = 22·4$, $[\alpha]_j = 191·8°$, and corresponding to the equation B.

$$\underset{\text{Starch}}{(C_{12}H_{20}O_{10})_6} + 2H_2O = \underset{\text{Maltose}}{(C_{12}H_{22}O_{11})_2} + \underset{\beta\ \text{Dextrin}}{(C_{12}H_{20}O_{10})_4}.$$

(*c*) When starch is acted on by malt extract at temperatures from 68-70°C. to the point at which the activity of the transforming agent is destroyed, if the solution be cooled and filtered at the end of five to ten minutes, the product contains maltose and dextrin in proportions agreeing closely with 17·4 per cent. of the former and 82·6 per cent. of the latter; $K = 11·3$, $[\alpha]_j = 202·8°$, and corresponding to equation C.

$$\underset{\text{Starch}}{(C_{12}H_{20}O_{10})_6} + H_2O = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + \underset{\alpha\ \text{Dextrin}}{(C_{12}H_{20}O_{10})_5}.$$

O'Sullivan considers that the formula for soluble starch must be at least six times the $C_{12}H_{20}O_{10}$ molecule, and that it, as well as the dextrins which are produced from it by the action of diastase, are a series of bodies of the same molecular weight in which the difference in their behaviour to this agent must be accounted for by a difference of relation in the arrangement of the molecules to one another, probably in solution alone.

In 1879 Brown and Heron (C. J. 35, 596), whilst confirming to a large extent O'Sullivan's results, came to the conclusion that the transformations of starch are to be represented by at least ten equations, of which they considered that their experiments substantiated at least four well-defined molecular transformations, by far the best-defined and most stable being the reaction obtained when starch paste is heated with malt extract at 60°C. for thirty minutes,

$$K_{3·86} = 49·3, \quad [\alpha]_{j3·86} = 162·5°$$

The next fixed point is that of the disappearance of the iodine reaction for erythro-dextrin when starch paste is transformed with malt extract heated to 66°C. This takes place when $K_{3·86} = 25·0$ and $[\alpha]_{j3·86} = 188·5°$ or thereabouts, and is very constant with varying quantities of malt extract.

The next strongly-marked reaction is that obtained with malt extract heated to 75°C., the numbers obtained being $K_{3·86} = 18·9$, $[\alpha]_{j3·86} = 195$-$196°$.

The highest stable transformation is obtained by the action of malt extract heated to 66°C. and made very slightly alkaline with sodium hydroxide, the same reaction being also marked in all transformations above 66°C. by the appearance of the maximum iodine colouration for erythrodextrin, the numbers for this transformation $K_{3·86} = 12·7$ and $[\alpha]_{j3·86} = 202$-$203°$ are very nearly those of O'Sullivan's equation C.

It was also found that when higher conversions are treated with unheated malt extract at

50–60°C. they are very rapidly converted into the lower form $K_{3\cdot86}$ 49·3°, $[\alpha]_{j3\cdot86} = 162\cdot5$, at which points these factors remain for a time constant.

Brown and Heron conclude that the dextrins are not metameric but polymeric bodies; those corresponding to transformations of high optical activity being of greater molecular complexity than those yielded by transformations of lower optical activity, the latter being produced from the former by a partial act of hydration with consequent elimination of maltose. About the same time Musculus and Gruber (Bull. Soc. Chim. 30, 69) brought forward a similar theory. They look upon starch as a polysaccharide, having for its formula $n(C_{12}H_{20}O_{10})$, and undergoing under the influence of diastase successive hydrations and decompositions.

As the result of their experiments Brown and Heron were led to adopt the formula $10(C_{12}H_{20}O_{10})$ for soluble starch.

The first action of the transforming agent upon this complex and unstable molecule results in the removal by hydration of one of the groups of $C_{12}H_{20}O_{10}$, thus producing maltose, whilst the remaining nine groups, $C_{12}H_{20}O_{10}$, constitute the first dextrin of the series, erythrodextrin *α*. This dextrin, in its turn, on further hydration splits up into a molecule of maltose and erythrodextrin *β*, consisting of eight $C_{12}H_{20}O_{10}$ groups, and so in this way the degradation of the original molecule proceeds, until by successive stages of hydration the lowest equation is reached. The following table represents these transformations:—

TABLE IX.

No. of Transformation	Maltose	Dextrin	$[\alpha]_{j3\cdot86}$	$K_{3\cdot86}$
Soluble Starch	0	0	216·0	0
Equation 1	10·4	89·6	209·0	6·4
„ 2	20·8	79·2	202·2	12·7
„ 3	31·0	69·0	195·4	18·9
„ 4	41·3	58·7	188·7	25·2
„ 5	51·3	48·7	182·1	31·3
„ 6	61·1	38·9	175·6	37·3
„ 7	71·0	29·0	169·0	43·3
„ 8	80·8	19·2	162·6	49·3
„ 9	90·3	9·7	156·3	55·1
Maltose	100·0	0·0	150·0	61·0

In 1879 Herzfeld (B. 1879, 2120) found that in addition to maltose and dextrin a third body, maltodextrin, was under certain circumstances formed by the action of diastase upon starch paste. This body was regarded by him as being intermediate between achroodextrin and maltose, but insoluble in alcohol of 90 p.c., and completely fermentable by yeast, possessing a specific rotatory power $[\alpha]_j = 171\cdot6$, $K = 23\cdot5$. This body has been further investigated by Brown and Morris (C. J. 47, 527). They find that when the action of malt extract on starch paste is limited there is always found amongst the products of transformation, besides maltose and dextrin, a third body which is more soluble in alcohol than the dextrins, and has a specific rotatory power of $[\alpha]_{j3\cdot86} = 193\cdot1$ and a cupric reducing power of $K_{3\cdot86} = 21\cdot1$, corresponding to an apparent composition of 34·6 p.c. maltose and 65·4 p.c. dextrin. It is completely hydrated to maltose by the action of malt extract at 50–60°C.

Maltodextrin is not fermentable by yeast (*S. Cerevisiæ* of the high fermentation), but is slowly hydrolysed into maltose and thus rendered fermentable by certain forms of saccharomyces of the secondary fermentation (*S. Pastorianus*, *S. ellipticus*). Brown and Morris consider that maltodextrin is not, as supposed by Herzfeld, a mere hydration product of achroodextrin, but that it is produced from starch and the polymeric dextrins by the fixation of a molecule of water upon the ternary group $(C_{12}H_{20}O_{10})_3$, of which there cannot be less than five in the starch molecule, which results in the separation from the dextrin residue of maltodextrin

$$\left\{\begin{array}{l} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{array}\right..$$

This by the fixation of two more molecules of water gives rise to freely fermentable and crystallisable maltose.

Further experiments in connection with this subject have induced Brown and Morris to alter their views with regard to the dextrins (C. J. 53, 610; 55, 450, 462; Trans. Lab. Club. 3, 81), which they consider are, after all, not polymeric but metameric, and from their investigations they have built up the following hypothesis, which appears to them to be more in accord with the facts than any other yet propounded.

The starch molecule may be pictured as consisting of four complex amylin groups arranged round a fifth similar group constituting a molecular nucleus.

The first action of diastase is to break up this complex group and liberate all the five amylin groups. The central amylin nucleus, consequent on a closing up of the molecule, withstands the further influence of hydrolysing agents, and constitutes the stable dextrin of No. 8 equation. The four outer amylin groups are capable, when liberated, of being rapidly and completely converted into maltose by successive hydrolysations through a series of amyloïns or maltodextrins, the number of which is only limited by the size of the original amylin group. This theory, which has not by any means gained universal acceptance amongst chemists who have studied the subject, appears, according to Brown and Morris, to embrace and explain all the known facts in connection with starch transformation.

Perhaps it is as well to call attention here to the fact that all the work mentioned above has been carried out with carefully purified potato starch, but it has been ascertained that similar experiments made with widely differing starches—such as maize, rice, wheat, arrowroot, sago, barley, and various other starches—practically yield the same analytical results when acted upon in the form of paste by diastase, but it has been found that the same starches differ materially from one another when the unbroken granules are acted upon in the cold, as will be seen from the following table by Lintner (Brauer und Malzkalendar [13] 83, 1890)[1]:—

Table X.—*Action of diastase on ungelatinised starch.*

Starch from	Temperature				
	50° C.	55° C.	60°C.	65°C.	70° C.
Potato	0·1	5·0	52·7	90·3	—
Maize	2·7	—	18·5	54·6	93·3
Rice	6·6	9·7	19·7	31·1	—
Oats	9·4	48·5	92·5	93·4	—
Barley	12·1	53·3	92·8	96·2	—
Green malt	29·7	58·6	92·1	96·3	—
Cured malt	13·1	56·0	91·7	93·6	—
Rye	25·2		93·7	94·5	—
Wheat	—	62·2	91·1	94·6	—

All the known digestive ferments belong to the class of soluble or unorganised ferments, and of these the properties of only seven are anything like accurately known up to the present. Only two appear to have any very marked action upon starch—these are the diastases of the saliva and of the pancreatic juice. The action of these diastases upon raw starch and upon starch paste is very similar to that exercised by the diastase of malt, with the exception that in addition to dextrin and maltose, dextrose is also formed, through the hydrolysation of the maltose by these ferments, the action on raw starches varying according to the kind of starch acted upon. (See Roberts, Digestive Ferments; Church, Food Grains of India; Bell, Chemistry of Foods; Brown and Heron, Pr. 1880, 393; Chittenden and Cummins, C. N. 51, 256; Chittenden and Smith, C. N. 53, 109.)

16. *Action of bacteria.* According to Fitz (B. 10, 276; 11, 42), starch yields by fermentation with a *Schizomycetes* (*Bacillus butylicus*, *Bacillus subtilis*) 35 p.c. of butyric acid and 9 p.c. of acetic acid, together with a small quantity of succinic acid. Inulin appears to yield the same products.

By the action of certain organisms, starch is rendered capable of being converted into dextrin and maltose, and eventually into alcohol. In this way the Indians of South America make an alcoholic liquor called *chicha* by the fermentation of the starch of maize. The grain is first allowed to soak for from four to six hours to soften it and afterwards fermented. The fermentation is due in the first instance to the presence of a minute organism, situated on the epidermis of the grain; this secretes a diastase, which either produces or aids further fermentation (Marcano, C. R. 95, 856).

Gayon and Dubourg (C. R. 103, 885) mention a species of mucor which has the power of converting dextrin and starch into sugar, and then fermenting the sugar.

Bacillus suaveolens converts starch gradually into dextrin and glucose, with formation of alcohol, aldehyde, formic, acetic, and butyric acids, &c. (Sclavo and Gosio, Arch. ital. Biol. 14).

Villiers (C. R. 112, 435 and 536) finds that the addition of a pure cultivation of *Bacillus amylobacter* to a 5 p.c. starch paste causes complete liquefaction in twenty-four hours, and on allowing the fermentation to continue some time the liquid no longer gives a blue colouration with iodine, the products of the change being almost exclusively dextrins, no maltose or dextrose being found to be present, from which he concludes that the organism converts starch directly into dextrin without the intervention of any diastase secreted by the ferment.

Perdrix (Ann. Inst. Pasteur, 1891, No. 5) has separated from Paris water a bacillus, *B. amylozymicus*, which ferments starch with production of dextrin, glucose, carbonic anhydride, ethyl and amyl alcohols, acetic and butyric acids. A somewhat similar change is effected by the bacillus of malignant œdema (Kerry and Fraenkel, M. 12, 350).

Manufacture of Starch.

17. *General considerations.* In growing various starch-producing plants for manufacturing purposes, the following facts must be taken into account: 1. The average percentage of starch contained in the root, tuber, or grain; 2, the yield per acre; and 3, the amount of starch yielded per acre. Thus, although the potato at best contains only 20 p.c. of starch; wheat, on the other hand, contains 55 p.c.; nevertheless the total amount of starch per acre is in favour of the potato, in the proportion of 2 to 1, since one acre of ground on the average produces 12,994 lbs. of potatoes, containing 2,598 lbs. of starch, as against 1,860 lbs. of wheat, containing 1,023 lbs. of starch.

Again, different varieties of the same species of plant will show very marked differences in the quantity of starch which they yield. For instance, the potato, as ordinarily consumed as food in this country, contains only about 13 p.c. of starch, but in Germany, where the potato is cultivated for starch production, by means of careful selection and suitable manuring the percentage of starch has been raised to as much as 20 p.c., and in some instances as great a yield as 24 p.c. has been obtained. The yield of starch is also affected by the age of the raw material, conditions of harvesting, and exposure to heat or cold during storage.

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[1] Cf. also Die stärkeumbildenden Fermente, Baranetzky, 1878, and Brown and Morris, C. J. 57, 510.

It has been found that over-ripe potatoes contain less starch than others, the loss being from 3·18 to 9·88 p.c. on 100 of starch (Kramer, B. C. 1881, 717).

A sample of barley, which had been exposed to bad weather for a fortnight, and had sprouted, was found to have lost an appreciable amount of starch, that in normal barley being 64·1, whilst that in the sprouted grain was only 57·9 p.c.

Diseased potatoes contain considerably less starch than sound ones, owing to its conversion into sugar by the fungus which attacks them, those tubers which are grown with the aid of highly-nitrogenous manures being more susceptible to the disease than those which are grown under ordinary conditions (Gilbert, Agr. Students' Gazette, 4, pt. 2). Exposure to extreme cold tends to diminish the amount of starch in potatoes, the generally-accepted idea being that by the freezing a portion of the starch is converted into sugar.

On the other hand, although the materials may be all that is desired, the yield of starch may be low, from causes due to carelessness in the processes of manufacture, such as insufficient washing or defective machinery, &c.

The raw materials almost exclusively employed in Europe and North America for the preparation of starch therefrom are wheat, potatoes, maize, and rice. Wheat was very generally used at one time, but has now been almost entirely replaced by the other substances. Potatoes are very largely employed on the Continent, rice principally in England, and maize almost universally in America.

The manufacture of starch may be classed under three heads.

1. For manufacturing purposes generally, such as the sizing of paper and of cotton goods, the dressing of cloth, the thickening of mordants and colours in calico-printing, the preparation of British gums, of white glucose syrups, &c.

2. For laundry purposes.

3. For edible purposes, either by itself, as in the preparation of cornflours, arrowroot, tapioca, &c., or in conjunction with other substances in the preparation of sauces, macaroni, semolinas, &c.

The extraction of starch from wheat and barley is one of the oldest processes known in the manufacture of starch, being employed by the ancient Egyptians, Greeks, and Romans. It was called ἄμυλον by the Greeks, from the circumstance of its not having to be prepared by the action of grinding in mills like other farinaceous substances, whence the Latin *amylum*. Very little, however, appears to have been known about its history or composition until the beginning of the last century.

18. *Manufacture of starch from wheat.* The different methods of preparing starch from wheat are:

I. By fermentation, and known as the old or sour process.

II. Without fermentation, or Martin's process.

I. Fermentation process. For the old method the wheat is used either whole or ground, but the whole corn most frequently.

Where the whole corn is employed, the wheat is steeped in soft water for some days, until it becomes swollen and so soft as to be easily crushed between the fingers; the water being changed frequently, so as to ensure, at the same time, a thorough washing of the grain. The swollen corn is now transferred to bags, and placed in a wooden chest or flat tub, where it is exposed to strong pressure. By this means the grains are crushed, and the water, which is rendered milky by the starch, is drawn off by means of a tap; fresh water is poured in, and the pressure repeated until all or nearly all of the starch is extracted. Instead of putting the swollen grain in bags, it may be passed from a hopper between two wooden cylinders revolving in opposite directions, or between one or two cylinders revolving upon a horizontal stone having a rim, to a cistern; by this means the swollen corn is readily crushed and the starchy liquor in the cistern separated by elutriation with successive quantities of water.

The milky liquor containing the starch is next run into cisterns, where it is allowed to remain for a period of from ten to thirty days, according to the temperature of the surrounding atmosphere, during which time it undergoes fermentation, in order to accelerate which some of the sour liquor from a previous fermentation is added.

By this means the starch granules become completely freed from the glutinous envelopes containing them in the grain, the gluten becomes more or less decomposed and softened, and partially dissolved in the acids formed during the process, and completely loses its sticky elastic properties.

During the earlier stages of the fermentation the ready-formed sugars of the grain, as well as dextrin resulting from the action of the diastase on any broken starch granules, become converted into alcohol, which later on is changed into acetic acid; after a few days lactic, butyric, and other fermentations are set up, and allowed to proceed until the process is considered sufficiently far advanced to allow of the starch granules being easily separated in a state of comparative purity. As a rule, actual putrefaction, as shown by the evolution of stinking gases, should be avoided as much as possible, and the fermenting mass should always have an agreeable vinous smell. During the process it is necessary to agitate the mass throughout once or twice a day, in order to equalise the fermentation as much as possible.

As soon as the fermentation is considered to have progressed far enough the supernatant liquor is drawn off and fresh water run in, the whole well stirred up, allowed to settle, and the surface liquor drawn off. This washing is repeated as long as any perceptible colour is imparted to the water; after the last deposition and decantation, the starch will be found to have settled down in layers of varying purity, the topmost one containing the most gluten and albumen. These different layers are now taken up with a wooden shovel, and transferred to separate cisterns, where they are agitated with water and then passed through fine sieves. After the starch has again settled down, the clean water is drawn off, any impurity that may be on the top separated, and set aside to be washed up with the next batch; the underlying portion agitated again with fresh water, and purified by settling and decantation, this being repeated as often as may be deemed necessary. When the starch is sufficiently white it is laid on linen cloths in wicker baskets to drain and become partially dry, or laid upon blocks of plaster of Paris, which absorb the moisture. When sufficiently firm and dry it is cut into pieces, which are spread upon other cloths and thoroughly desiccated in a proper drying-room, which in winter is heated by stoves.

Or the starch, after being sufficiently purified by successive washing and decantation, may be shovelled into wooden boxes about 4 feet long, 12 inches broad, and 6 inches deep, perforated throughout and lined with thin canvas; this is termed 'boxing.' When it has drained and dried into a compact mass, it is turned out by inverting the box upon a clean table, where it is cut up into pieces 4 or 5 inches square; these are then set upon half-burned bricks, which by nature of their porosity absorb the moisture from the starch, so that the under surface of the blocks may not become hard and horny.

When sufficiently dried upon these bricks, the blocks of starch are put into a stove and left there until tolerably dry; they are then removed to a table, where all the sides are carefully scraped with a knife, next packed up in the paper in which they are sold, returned to the stove, and subjected to a gentle heat for some days, previous to being sent into the market.

II. Martin's process. In this process flour is employed in preference to the whole or crushed grain. It is kneaded into a stiff dough with water, exactly as for bread-making, and allowed to remain in that state until every part becomes thoroughly saturated with moisture. This requires 25 minutes in summer and about an hour in winter. For the separation of the starch from the gluten an apparatus is employed, consisting of two troughs which are similar to each other, and which may be of any convenient length. Within each of these troughs there is a rectangular frame, which is caused to move to and fro within the trough by a crank axis and connecting rod, the crank of one trough being set opposite to that of the other.

Each of the frames carries the bearings of four or other convenient number of grooved rollers. At the bottom of each of the troughs there are openings at intervals covered with wire gauze; at the ends of each trough are applied spring buffing apparatus. Below the troughs is an inclined sieve of fine wire gauze, and below it an inclined shoot, down which the fluid which passes the sieve flows, and from it into any suitable receiving vessel, where the starch is allowed to settle; above each trough there is a perforated pipe, through which the numerous jets of water flow on to the dough introduced into the trough, and which serves to wash away the starch from the gluten.

The dough which is to have the starch separated from the gluten is formed into small balls, and placed in the troughs between the rollers. The frame carrying the rollers is caused to reciprocate, a constant spray of water being allowed to flow over the dough at the same time, by which means the starch is washed out and separated from the gluten; the milky liquor flows through the openings in the bottom of the trough on to the inclined sieve, and thence by means of the shoot to a suitable receiving vessel. Should any particles of gluten pass through the openings, they pass along the inclined sieve, and are received in a vessel. After the dough has been subjected for a sufficient length of time to the action of the rollers, it consists for the most part of gluten, and is placed between the ends of the frames and the buffing apparatus, where it is beaten for several minutes, and can then be used for any purpose to which it is applicable.

The purification of the starch obtained in this way may be effected in the usual manner, by successive washings and decantations as in the fermentation process, or by the inclined plane method described below under potato starch. Subsequently, Martin introduced the following process for the purification of the crude starch, whereby a better product is obtained than is possible through mere washing with water. This consists in treating the impure starch with a weak solution of sodium hydroxide, sp. gr. 1·013, in sufficient quantity to turn red litmus paper blue, after the deposit has been well roused up. The mass is then allowed to stand for two hours, during which time the gluten swells up, and becomes partly dissolved. A considerable quantity of water is then added, and the whole thrown on to a No. 200 sieve, which retains the swollen gluten and allows the starch to pass through, which is then run on to the inclined plane as before. Almost the whole of the starch is by this means obtained as a first product, whilst with simple washing about 25 p.c. is produced in an impure, unmarketable form.

On the average, there is obtained from a sack of flour about 110 lbs. of moist gluten and about 220 lbs. of dry starch.

19. *Manufacture of starch from potatoes.* At one time the manufacture of starch from potatoes was carried on to a certain extent in Great Britain as well as in Ireland, the first published specification relating to starch being taken out as far back as the year 1717 by Newton, Nowell, Clark, and Joynes, for 'a way or method to make starch of and from the roots called by the name of potatoes,' but its development has been considerably checked by the potato disease, and is now entirely replaced by starch from rice.

In France and Germany, however, where much more attention has been directed to the growth of the potato as a starch-producer, the manufacture of fecula or starch from this source has attained very considerable dimensions and large quantities of potato starch are imported yearly from those countries.

On the Continent the manufacture of potato starch, for an account of which the writer is much indebted to Payen's Chimie Industrielle, includes the following operations—steeping, washing, separation of stones, rasping, straining, settling, removal of the starch, purification, second straining, washing, draining, and drying in the air or in a centrifugal machine, drying in an oven, packing.

Steeping. Potatoes which are grown in tough clay or loam are covered with adherent earth, which clings so tenaciously to them as not to be removed by simple washing; they are therefore allowed to soak for several hours in a large vat containing water.

Washing. In France this operation is carried on as follows:—An apparatus called the washing drum (fig. 1) is used, consisting of a hollow revolving cylinder *b*, formed of wood or iron bands, $\frac{1}{2}$–$1\frac{1}{2}$ inches wide, and laid longitudinally from one end to the other, the distance between each being about $\frac{3}{4}$ inch, so as to allow of the escape of the dirt, sand, and stones, whilst the tubers are retained. The cylinder, which is slightly inclined, is immersed to half its diameter in water in the trough *c*, wherein it revolves at the rate of about fifteen revolutions per minute, and by which means the potatoes are kept in continual motion, rubbing against and being rubbed by the sides of the cylinder. From the sides of the trough spring the boards *g*, slanting to the upper part of the cylinder, so as to prevent splashing of the water. The cylinder is worked by a band from the main shaft, passing over the wheel *f*. The potatoes are fed into the hopper at *a*, and are thrown out at the opposite end, where, falling down the inclined plane *d*, they are conducted to the stone catcher (fig. 2). This apparatus consists of a semi-cylindrical sloping trough, filled with water to the level A. In the trough is a shaft D, furnished with arms placed spirally (figs. 3 and 4), and which by means of the cogwheel E is rotated by the driving wheel F. The potatoes being fed in at A, are rubbed upon one another by the arms and repeatedly dipped in the water, so that the remainder of the dirt and all stones and sand is washed off, and, the heavier particles sinking to the bottom are removed from time to time through the opening C. The potatoes are carried forward by the action of the spiral until they reach the upper end of the trough, over which they fall into the hopper of the rasping machine.

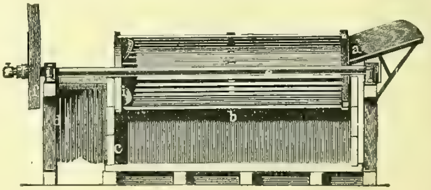


FIG. 1.

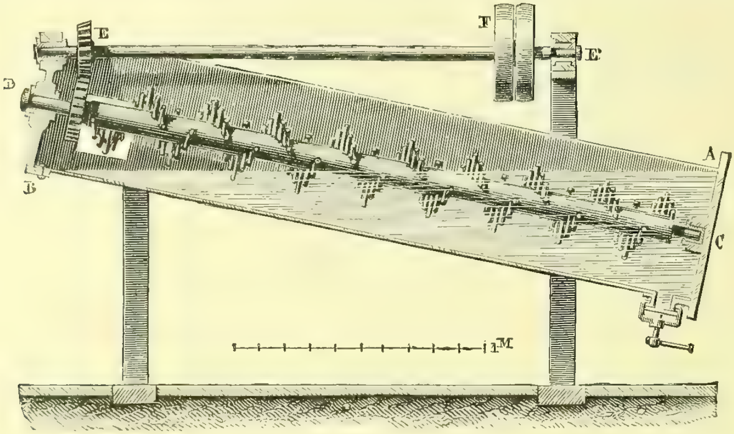


FIG. 2.

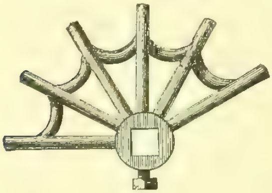


FIG. 3.

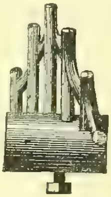


FIG. 4.

In the German factories the above operations are carried on at one and the same time, the trough in which the washing drum is placed being divided into two unequal parts, the larger one *d* for the washing drum, and the other *e* for the stone catcher; as shown in figs. 5 and 6, the potatoes are introduced into the smaller division *e*, and are drawn forward and kept in incessant motion by six or eight large iron arms *gg*, arranged spirally on a prolongation of the shaft of the washing drum *a b*. The stones, sand, &c., are drawn off at intervals through the openings *i* and *h*. The potatoes thus reach the washing drum previously washed and freed from stones, from which they pass through *k k* to the rasping machine.

By means of this the tubers are reduced to a pulp, and the cells containing the starch are ruptured; and the more completely this is done the greater the amount of starch obtained, since it is only the starch from the cells which are actually ruptured that can be extracted, whilst all that remains in closed cells represents so much loss to the manufacturer. For this purpose Champonnois' rasper is generally considered the best, and is shown in figs. 7 and 8. It consists of a hollow cylinder furnished with saw blades on its inner surface, against which the potatoes are made to rub. The case A of the cylinder is seen in fig. 8, with the rasper inside. This is so arranged that from one to four saw blades lie between thin steel bands, at an interval of from $\frac{1}{50}$–$\frac{1}{25}$ of an inch apart, and between each group is a space through which the pulp as it is formed can pass. This arrangement is shown in figs. 9 and 10. In the axis of the rasping cylinder is a shaft B B, making 800 to 1,000 revolutions per minute, by means of a band from the main shaft applied to the driving-wheels E E, and regulated by a fly-wheel. At the other end of the shaft, within the drum, is a strong fork-shaped scoop. The potatoes, falling through a side opening, are seized by the scoop, and pressed forcibly against the saw blades C C in the cylinder. Water, being admitted into the interior, is driven by centrifugal force against the sides of the cylinder, and makes its way through the interstices, carrying with it the potato pulp, which passes away through a pipe underneath. The teeth of the saw blades are very short, projecting one-fifth of an inch from the drum. They require reversing twice a day, and after two days' use need to be re-filed. As much as thirteen tons of potatoes can be rasped by this machine in ten working hours, whilst the yield of starch from a given quantity of potatoes is considerably increased.

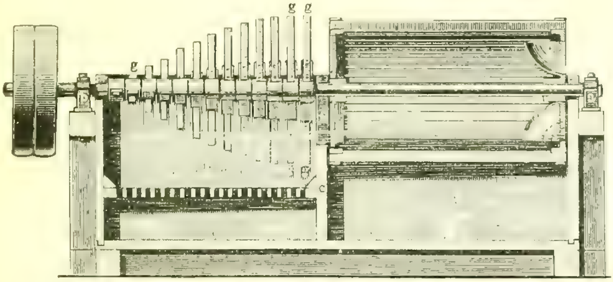


Fig. 5.

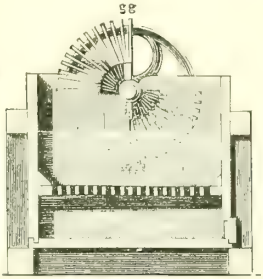


Fig. 6.

Fig. 7.

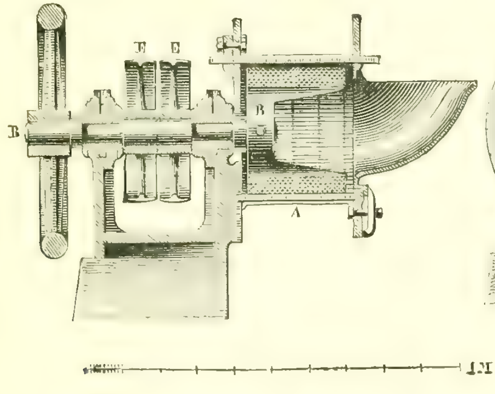
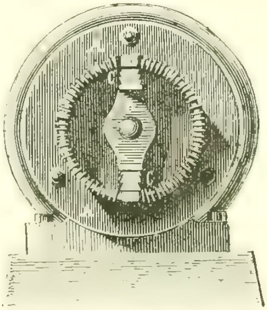


Fig. 8.



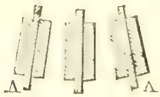


Fig. 9.

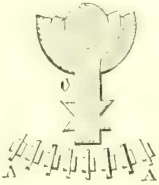


Fig. 10.

The pulp thus obtained is a mixture of starch and fibre. In order to separate one from the other the pulp is washed with water upon brass-wire sieves of different degrees of fineness, which allow the starch granules to pass through with the liquid and retain the coarser portions of the fibre. Several forms of apparatus have been devised for this purpose, the principal objects aimed at being uninterrupted working, as complete exhaustion as possible of the pulp within the smallest space, and economy of wash water. Fig. 11 shows a longitudinal section of Huck and Stoltz's machine. This consists of three cylinders A, B, C of different diameters. The case of the first is formed of a wire sieve, 25 meshes to the inch. The pulp from the rasper is run in through the funnel *a*. Within this cylinder is another, *bb*, formed of perforated metal plate into which water flows through the pipe a'', and is distributed uniformly upon the potato pulp in A by means of the perforations in *bb* from A. After parting with the greater part of its starch the pulp is gradually brought forward into the second cylinder B, which is covered with sheet copper. The pulp is here worked about with a T-shaped iron fastened to the shaft DD′, which is rotated by the driving wheel G in an opposite direction to the cylinder; from here it is carried forward to the third cylinder, which is covered with wire tissue, 35 meshes to the inch, where it meets with a fresh spray of water coming through the perforated pipe *dd* from a'''. Whilst in the cylinders A and C the pulp undergoes a continual working with brushes, which, like the agitator in B, are connected with the shaft DD′. These three cylinders revolve at the rate of 22 revolutions per minute; whilst the agitator in B makes 35 in the same time. The starchy liquid flowing from A and C is collected in the trough K, and runs from thence into the sieve cylinder HH′, which is covered with wire gauze, 50 meshes to the inch. Here any fibrous pulp which may have passed through the other sieves is retained; whilst the water containing the separated starch is run off along the trough L into the settling vats. The coarse pulp as it is pushed out of the cylinders falls into the receivers MM′ underneath. In order to prevent the clogging of the sieves, a fine stream of water is thrown upon them during working from pipes running parallel with their axis.

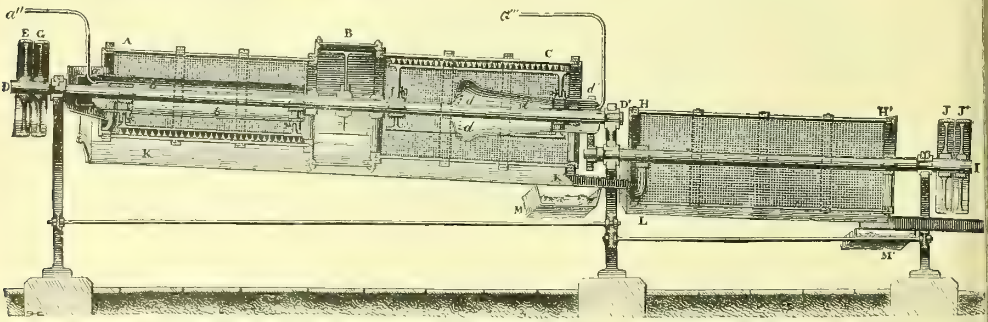


Fig. 11.

A modification of the above apparatus, by means of which considerably less water is required, and which is suitable for localities where water is more or less scarce, is shown in fig. 12.

The pulp coming from the rasper A is raised by means of a centrifugal pump into the first cylinder B, where it gives up by far the greater part of its starch. The strained liquor from this cylinder is not joined with that from the other cylinders, but run straight away into the purification vessel. The liquor from the mixing cylinder C and the other sieve cylinder D, containing comparatively but little starch, is carried by the pipe GG′ back to the rasper, where it is used instead of clean water for the thinning of the pulp.

In some factories, by means of a modification of the apparatus just described, a second working of the pulp is effected, and a larger yield of starch thereby obtained. This is shown in fig. 13. The pulp, thinned with water, falls from the rasper A into a small cistern, from which it is raised by the pump B, through the pipe B′, into the sieve and mixing cylinders D, D′, D″, and in the latter washed by a stream of water a'. The pulp rejected from D″ falls into the hopper of a second rasper, where it is rubbed between two cylinders F rotating in opposite directions; from thence it flows into the sieve G, where it meets with more water from a''', and, being washed, falls into a trough, along which it is pushed by an Archimedean screw.

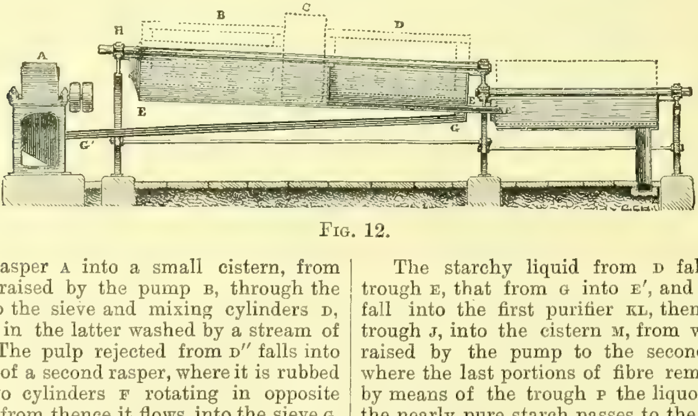


Fig. 12.

The starchy liquid from D falls into the trough E, that from G into E′, and both united fall into the first purifier KL, thence into the trough J, into the cistern M, from whence it is raised by the pump to the second purifier O, where the last portions of fibre remain, whence by means of the trough P the liquor containing the nearly pure starch passes to the purification apparatus. In the smaller factories this is generally accomplished by means of settling vats.

In addition to rasping, a great many manufacturers are accustomed of late years to grind the pulp after rasping, whereby a slightly increased yield of starch is obtained. The following figures, calculated on the starch worked,

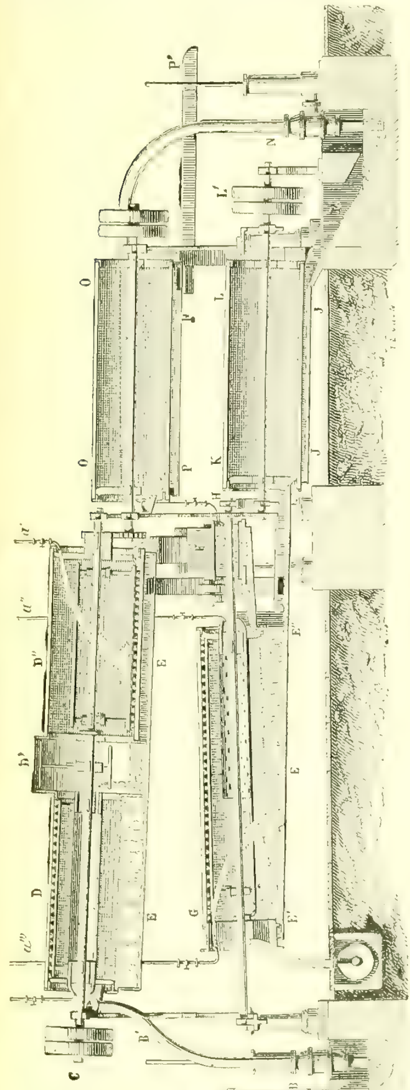


FIG. 13.

show a comparison between the yield obtained when a rasping machine only is employed, and when, in addition thereto, grinding is carried on as well.

Obtained in form of green starch	Without grinding	With grinding
Experiment A. . .	81·8	87·4
Experiment B. . .	76·3	85·5

Various forms of machines for carrying on the rasping and grating processes simultaneously have been constructed during the last few years, but have not up to the present come into general use.

The starchy liquor as it comes from the sieves generally contains some sand, which was not separated during the washing of the potatoes, and was too fine to be retained by the sieves. It is therefore run into a large vat and vigorously stirred so as to bring all the starch into suspension, which, before it has had time to settle, is siphoned off into another large vat, where it is allowed to stand for four hours, during which time the starch settles on the bottom. The sand, by reason of its greater specific gravity, sinks rapidly to the bottom, and remains in the first vat. The lower part of the sediment deposited in the second vat consists of pure starch, covered by a greyish layer, consisting of fine fibres that have passed through the sieves. The supernatant liquor having been run off, this impure mass is scraped off as clean as possible with an iron scraper. This impure starch is agitated with fresh water, passed through a very fine sieve, and allowed to rest for some time, till a further amount of white starch falls out, when the same operation is repeated.

The purified starch is again agitated with water, passed through a silk or wire sieve, 90 meshes to the inch, and again allowed to settle, the liquor decanted off, the surface of the starch scraped, and finally, if the mass be pure enough and of sufficient consistence, divided into lumps and placed to dry.

Sometimes the starch, deprived of its supernatant brownish deposit, is purified by being placed in a slightly sloping flat-sided trough about 22 feet long and 3 feet wide. Below this is a second trough, inclined in the opposite direction; and below this a third, inclined like the first. A spray of water from a very fine rose falls upon the starch, which is placed just beneath it at the top end of trough No. 1, and at the same time is kept constantly stirred. The water gradually washes everything forward with it, and while slowly flowing along the troughs the starch is gradually deposited; whilst the lighter fibrous matter remains in suspension, and passes with very little starch into vats underneath. The starch obtained in this way is added to that purified in the first settling vat, and is then ready for draining.

In large factories the settling vats have been entirely superseded by the inclined plane; this consists of a series of three wooden troughs, fig. 14, $3\frac{1}{2}$ feet wide and about 30 yards long, each having a fall of 1 to $1\frac{1}{2}$ in 1,000. The third plane or trough rests on the ground and empties into the vat G. The second and first are affixed to wooden supports as shown. The starchy liquor, as it comes from the cylinder sieves, enters the first inclined plane at A, flows along in the direction A B, and thence along C D to F, the flow being regulated at will by means of the screw valves at B and D. The greater part of the starch is deposited in the first plane, from which it is removed once a day. The starch from the second plane, on which considerably less is deposited, is removed twice a week; and once a week, from the third. The liquor, containing very little starch, flows into vat G, or generally into a series of vats, whereby any starch that may still remain in the wash water is collected.

The starch thus deposited on these inclined planes is sufficiently pure for most purposes to be sent at once to market; but, as it is still contaminated to a slight extent with potato sap, in order to purify it completely it is advisable to wash it once or more in the usual settling vat.

Drying. The starch is taken from the planes or settling vats in the form of a very thick mud or sludge, from which the greater portion of the water may be removed by centrifugal action, by drying in the air or in ovens.

In the drying of starch by centrifugal action the same form of apparatus is used as in the manufacture of sugar, but as the starch mud is so thick as to render it incapable of being properly distributed on the sides of the machine, a quantity of water is mixed up with it to bring it into a sufficiently thin paste that will flow into the apparatus whilst it is in motion. It is then flung against the circumference of the machine, the water flies off, and the starch lies as a compact mass round the sides of the cylinder. Advantage has been taken of centrifugal action for the purification, as well as for the drying of starch at the same time, by Fesca, of Berlin. When the impure starch liquor is introduced into the machine, the densest and heaviest portion—and consequently the purest starch—is driven first against the sides of the cylinder. The fibrous portion remains longer suspended, and is deposited as a layer upon the surface of the pure starch, from which it is easily removed.

For many purposes—such as the manufacture of dextrin and glucose, &c.—the starch, as it comes from the centrifugal machine, and containing from 35 to 40 p.c. of water, needs no further desiccation, and is known in commerce as green starch.

In factories where a centrifugal machine is not used, the water is removed as much as possible from the starch before proceeding with the drying. Accordingly, as soon as the starch is considered sufficiently purified, it is dug out of the settling vats and transferred to perforated boxes, lined with clean linen, and set aside for some time to drain, during which time it acquires sufficient hardness to enable it to retain the shape of the box, and as soon as ever this takes place the box is inverted upon a dry porous slab, generally of plaster-of-Paris, which abstracts a further amount of moisture, so that it arrives at the state of green starch. It is now sufficiently solid to be removed to the drying room, on either side of which a series of shelves, formed of bars of wood placed at a distance of about one inch apart, are ranged in tiers one above the other, through which a current of air is made to pass freely by means of louvre boards or venetian ventilators. On these shelves the blocks of starch are placed, and allowed to remain for six or eight weeks, until sufficiently dried. One great drawback to this method is the exposure of the starch to any dust that may be floating about in dry weather, as well as the possibility of the moist starch becoming frozen in cold weather. The latter may be obviated by introducing heated air into the drying-room, and the dust precluded by shutting up all the windows—in fact, by practically converting the room into an oven.

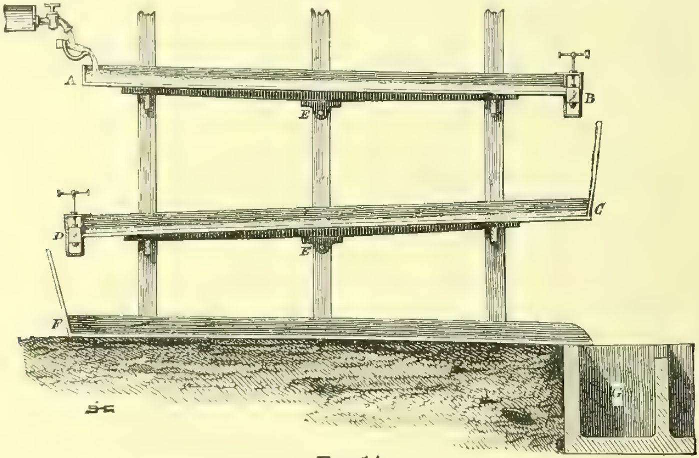


Fig. 14.

20. *Manufacture of starch from rice.* Although no other starch-producing material is so rich in this substance as rice—containing, as it does, over 80 p.c. of starch—nevertheless, the cells and the starch granules contained in them are so intimately connected together by a small but very resisting quantity of gluten that their separation cannot be effected by a simple crushing and washing, as in the case of potatoes, or by the old system of fermentation, as in the case of wheat and flour, and hence resort must always be had to chemical agents, alkalis or acids, to effect this object.

Since rice starch, on account of the smallness of its granules, possesses a greater firmness, and in practical operations gives a much higher lustre than wheat starch, it is much esteemed by laundresses, and preferred by them to any other, so that when the difficulties attending its successful preparation had been overcome, a wonderful impetus was given to its manufacture in England, where it is at present carried on to a very large extent, and, being cheaper in this country than any other raw material, may be considered as a fairly remunerative business.

It need hardly be said that the value of any sample of rice for starch manufacture depends not only upon the amount and quality of the starch it contains, but on the percentage of gluten or protein matter as well, and on its degree of solubility in soda solution.

The following analyses of rice from different countries show the relative amounts of these substances which are generally present in the matured grain:—

Analyses of rice.

—	Patna (Polson), cleaned	American (Jenkins), mean of 10 analyses	Japan (Kellner), mean of 10 analyses
Carbohydrates	81·81	79·20	74·10
Albuminoids	7·22	7·40	6·13
Fat	0·09	0·40	2·00
Fibre	0·18	0·20	4·00
Ash	0·90	0·40	1·19
Water	9·80	12·40	12·58

The method of manufacture described by Jones (Eng. Pat. 1840, No. 8,488)—and which is, with a few modifications, the one carried out at the present time in England—is as follows.

One hundred pounds of rice are placed in a tinned copper or stoneware vessel holding 50 gallons of a solution of sodium or potassium hydroxide, containing 200 grains of alkali per gallon of water; the mixture is well stirred and allowed to macerate for twenty-four hours, at the end of which time the liquor is siphoned off, and the rice well washed with twice as much cold water as there was of alkaline solution. The water is next poured off, and the grain placed upon sieves to drain, after which it is crushed or ground to flour with rollers or millstones. The flour is then passed through sieves by means of brushes, the coarser particles which do not pass through being returned to the mill to be reground and again sifted, until the whole is thus disposed of.

The flour thus obtained is again treated with alkali solution, one hundred pounds of the rice flour being added in small quantities at a time, to every hundred gallons of liquor. The whole is well stirred up repeatedly during twenty-four hours, and then allowed to stand for about seventy hours to settle. The process of this deposit takes place as follows: the first deposit consists of fibrous matters with little starch, followed by a deposit of the greater portion of the starch, the gluten and other matters remaining in solution in the alkaline liquor, which is siphoned off, and double as much water run on, the deposit is then well roused up with it, and the whole allowed to stand about an hour, during which time the matters other than starch subside, carrying with them a small portion of the starch, but leaving by far the greater bulk of it suspended in the liquor. This is drawn off, and passed through fine silk sieves. A further quantity of water is added to the deposit and agitated as before, and, after standing a short time again drawn off, and passed through sieves as before, this operation being repeated as often as necessary, until at length the whole of the starch is separated from the fibrous and other matters.

All these starchy liquors are then collected into one vessel and allowed to settle for about seventy hours, during which time the whole of the starch is deposited. The supernatant liquor is now drawn off, and the starch (blued if necessary) drained, dried, and finished in the usual way.

Several other patents for preparing starch from rice have been taken out by various manufacturers, the principal of which are the following:—

Berger's process (Eng. Pat. 1841, No. 9,013).—By this method: 1. Starch is manufactured from rice by the application of an alkaline salt, *e.g.* carbonate of soda, whereby the gluten is dissolved or freed, so that the starch may be separated therefrom. The operations are in all respects analogous to those of Jones' process.

2. The rice is soaked in water and submitted to a process of fermentation; or

3. The first and second processes are combined.

Colman's process (Eng. Pat. 1841, 2,166).—1. Rice is mixed with the refuse from wheat or other grain in the proportion of fifteen pounds of the latter to every hundredweight of rice, and, the necessary quantity of water being added, the mass is allowed to ferment for ten to fifteen days, after which the starch is separated by washing and sifting as already described.

2. The rice is steeped in water for four days, then drained, and reduced to a pulp in a mill under a stream of water, collected in a reservoir, allowed to settle, and the water siphoned off.

The deposit is then agitated with a dilute solution of hydrochloric acid (about 2 p.c.) and allowed to stand for five days, being well stirred every four hours during that time, then allowed to settle for eighteen hours, the clear liquor drawn off, and the operation repeated with a ·5 p.c. acid solution. Finally, the deposit is washed with large quantities of water, passed through sieves, drained and dried in the usual way.

Rehe patented a process (Eng. Pat. 1884, 10,359) according to which the rice is first submitted to a temperature of 160° to 180°F. before steeping, and afterwards macerated in soda lye (four pounds of soda to every hundredweight of rice), and the starch extracted in the usual manner later on.

Ransford introduced a process (Eng. Pat. 1853, 603), in which pressure is applied to the rice after it has undergone the steeping operation. The rice having been put into the steeping liquor, in a vessel capable of being closed down, is allowed to steep for some time. The vessel is then closed down tight and more liquor forced in by means of a pump, up to about 20 lbs. to the square inch; this is continued for a short time, the liquor drawn off, and again pumped in. The liquor is then drawn off, and the rice further pressed so as to drive out as much gluten as possible, after which it is ground and treated in the usual way.

In Germany the manufacture of starch from rice has replaced wheaten starch to a large extent, and J. Berger, who appears to have given much attention to this subject, has published an interesting account of the process as carried out there at present (Chem. Zeit. 14, 1440, 1571; 15, 843), an abstract of which is given below.

The raw material principally employed in Germany is obtained from rice-cleaning and polishing-mills, and consists of the broken grains. The percentage composition of various samples of this waste is given in the following table:—

—	East Indian rice			Russian rice	Egyptian rice	Persian rice
Water	12·10	13·20	13·23	12·70	11·84	10·80
Starch	76·25	73·90	77·44	75·81	78·30	73·20
Protein	8·95	8·79	6·87	7·94	6·70	11·21
Fat	0·42	0·71	0·35	0·40	—	0·75
Gum and sugar	0·86	1·20	0·95	1·21	—	1·45
Fibre	0·32	0·40	0·36	0·44	—	0·81
Ash	1·10	1·80	0·80	1·45	1·16	1·78

Extraction. The operation for the extraction of starch is carried out in shallow tanks of 4–5 cm. capacity. The rice is piled on a perforated shelf fixed in the tank, and covered with soda lye of 0·5° to 1°Bé. The mixture is stirred a few times, and after about eighteen hours the lye is run off and replaced by a fresh lot, which is allowed to remain for twelve hours, by which time the rice is, as a rule, sufficiently softened to be ground; this is effected between millstones 1,200–1,400 mm. in diameter and 300–400 mm. thick, and making 120 to 140 revolutions per minute. Incomplete grinding must be avoided as much as possible, and therefore in most factories the rice is passed through two mills arranged side by side, so that the ground starch drops directly from the first into the second mill. During grinding, the rice is moistened with lye of the same strength as that used for softening, about 200 litres being required per 100 kilos of rice. The starchy liquor flowing from the mill, and containing about 20 to 28 p.c. of solid matter, is carried up by suitable means to high-lying tanks, from whence it is distributed to the sieves and other apparatus.

Sieves. Rotating cylindrical sieves are almost invariably employed, and are constructed as follows: A shaft, 4–5 metres in length, is provided at intervals of 1 metre with three rods of equal length, arranged symmetrically at right angles to the shaft. The ends of these rods carry six wooden boards parallel to the shaft. The framework thus formed is covered with the finest silk gauze. The cylinder is so arranged that one end of it lies about 15 cm. higher than the other. The liquid to be strained is fed into the upper part of the apparatus. The starchy liquor, as it filters through, is collected in a wooden casing, which completely surrounds the cylinder, whilst the impurities remaining on the sieve pass along into a tank opposite the lower end of the cylinder. The shaft of the cylinder being hollow, and pierced with numerous holes, allows water to be forced through on to the sieves. By this means the walls of the cylinder are kept clean, and the passage of the impurities towards the lower end is facilitated. The starchy liquor passing through the sieves still contains much gluten, which may be separated in the manner described under *Potato starch*, either by means of settling tanks, or with the centrifugal machine.

Berger suggests many improvements in the above process. Great stress is laid upon the importance of the preliminary softening of the rice with a solution of caustic soda, as the precise action of the soda has been misunderstood by most rice-starch manufacturers, being generally regarded as a mere mechanical one instead of a distinctly chemical one, the soda dissolving out the albuminous substance which cements the starch cells together, thus rendering them more amenable to the after-operations. This softening process should be carried out as quickly as possible, especially in warm weather, in order to prevent fermentation, the evil effects of which are to be seen in all the after-processes. It causes the mass to froth excessively in the grinding-mill, and renders centrifuging difficult, the starch not separating as it ought to do in a state of purity, coming from the centrifugals in flabby lumps; and, for the same reason, it refuses to deposit in the settling tanks. The gluten assumes a slimy condition, and retains much starch. In order to obviate this, Berger recommends that the extraction and softening of the rice be effected by a continuous current of slightly stronger lye ($1\frac{1}{2}$°Bé.), as by this means the treatment is considerably shortened, and at the same time the action is rendered more energetic.

Another method proposed by Mack (D. P. J. 256, 35), and which has been successfully adopted in Germany, consists in blowing air under pressure through the mixture of rice and caustic soda in such quantities that the liquid assumes the appearance of boiling. For this purpose air enters through a series of small tubes into a tank provided with a false bottom, on which finely-ground rice is spread, the tank at the same time being filled with the soda solution. After the operation is finished the liquor is run off, and the resulting rice starch allowed to drain. By this process the rice is said to soften quicker, and yields from 6 to 8 p.c. more of the finished product.

When the various processes are employed in the order given, the yield of starch of the first quality is about 60 p.c. (calculated as absolutely dry starch on the rice), whilst 7–10 p.c. are left in the various by-products, and may be recovered by repeated treatment.

The total yield in a properly conducted factory is about 85–90 p.c. of the starch contained in the rice.

Moulding the starch. Formerly this was almost exclusively done in wooden boxes with perforated bottoms covered with filtering cloth. The boxes are set up in rows, and the starch mixed with water or weak soda lye (0·1° to 0·3 Bé.), being charged into the first box, overflows into the next, and so on. In order to make the water drain out more thoroughly, the boxes are repeatedly lifted from their supports and dropped again. After about twenty-four hours the blocks of starch, still containing 42–44 p.c. of water, are removed, and cut into rectangular pieces. Various forms of high-pressure filtering moulds are now employed, and with these the starch-milk used for filling must not exceed in specific gravity 1·2–1·25, otherwise the finished product exhibits a rough fracture which detracts from its appearance.

Drying the starch. Blocks of starch, containing 40–45 p.c. of water, when dried, become covered with a yellow crust, owing to the separation of traces of dextrin, &c. This crust is about 10 mm. thick, and is cut off when the blocks are partially dry—*i.e.* contain 25–28 p.c. of water. The remaining starch may be now completely dried without any further development of yellow colour taking place. All attempts hitherto made to avoid this crust formation have failed. The crust constitutes about 20–30 p.c. of the total starch. The shavings are stirred up with water, centrifuged once, or filtered, and mixed with the following batch of pure starch. Large masses of starch, when dried, fall into more or less irregular rod-like pieces, the size, shape, and smoothness of surface of which depend greatly on the rapidity of drying and the solidity of the blocks before drying. Starch is generally coloured in order to hide its slightly yellow tint, ultramarine being usually employed for the purpose. The blocks remain in the drying chamber for fourteen to twenty-one days, according to the temperature, which ranges from 30–50°C. The dried starch contains about 12 p.c. of water, but on exposure to air it absorbs moisture up to 15 p.c., which is the commercially recognised standard. If it be desired to obtain the starch in large lumps, the blocks, after scraping, are cut up into smaller pieces, which are then slowly dried in the air.

Waste products. These consist of gluten and impure starch. They may be mixed, and used for cattle-feeding; or, more or less separated and utilised, the starch for feeding, and the gluten for manurial, purposes.

21. *Manufacture of starch from maize.* This process is principally confined to the United States, and no industry in that country has grown so rapidly and concentrated itself into a small circle of factories within the last half century as the manufacture of starch from maize or Indian corn, which is there termed corn-starch. An nteresting account of this industry is given by Dr. G. Archbold, in S. C. I. [6] 80–84, of which the following is an abstract:—

The following analysis of maize, as given by Dr. Archbold, represents the average of many samples analysed in the course of one year's working:

Water	11·2
Starch	54·8
Cellulose	16·4
Gum and sugar	2·9
Gluten	8·2
Fat	4·7
Ash	4·8

Process of manufacture. The process universally adopted in the United States is that known as the alkaline or 'sweet' process, in contradistinction to the 'sour or acid' process adopted for the extraction of starch from wheat.

In the extraction of starch from maize by the 'sweet' process, the corn is first subjected to a cleansing process by means of powerful fans or blowers, called winnowing, by which means the grain is cleansed from superfluous bran, dirt, cob, &c. The clean grain is next placed in tanks called 'steeps,' or large tanks varying in capacity from 1,000 to 6,000 bushels each. Here the corn is covered with water at a temperature ranging from 70°F. to 140°F., according to the experience of the manufacturer, and allowed to remain until the grain is sufficiently soft to crush or grind between rollers. As it is of the utmost importance to the after-treatment of the impure starch that as much as possible of the oil and mineral constituents of the corn be removed, and the nitrogenous matter surrounding the starch of the grain, such as gluten and albumen, be thoroughly softened, so as to be brought to a condition to be acted upon by the alkali, the process of steeping the grain is one of great importance, and various methods have been adopted. In most factories the corn is allowed simply to remain in contact with the water for a period of eight or ten days, or until the putrefactive fermentation has set in, and the corn soft enough to grind. During this period much sulphuretted hydrogen is given off, thereby creating a most offensive odour in the neighbourhood of the factory.

At the Glen Cove Starch Works, Long Island, N.J., this disagreeable part of the process is obviated by adopting the Durgen system. In this factory there are three 'steeps' or tanks, each capable of holding 5,500 bushels, or 310,800 lbs. of corn. Through each of these tanks a continuous stream of water, heated to a temperature of 130–140°F., flows at the rate of about 10,000 gallons per tank per day, for three days, at the end of which time the corn is sufficiently softened for the grinding process. It has been estimated that no less than 315 lbs. of solid matter per day is extracted from all these tanks during this process, and which may be divided into

	lbs.
Oil and other organic substances	128
Albuminoids	61
Ash of corn and constituents of the water	126
Total	315

In this wet and softened condition the grain is conveyed to the grinding room, where it is first ground in burrstone mills, and thence passed through heavy iron rollers to wooden spouts, and carried by means of hoppers to the straining department, which is generally situated on the floor underneath the mills. These strainers consist first of large revolving sieves on a slight incline. The first series is of brass wire sixty meshes per square inch; the second of fine bolting silk, such as is to be found in flour mills. The ground pulpy mass falls with a stream of water into the first series, and then through the second into the collecting tanks below. The mixed fine and coarse magma which falls from the end of these sieves is then conveyed to the mills, re-ground, and again passed through these sieves with a stream of water as before, until the water ceases to come through milky. The magma thus exhausted of its starch is then conveyed to a separate room, and pressed, dried, and sold as cattle food, or in its moist condition as 'swill' for pigs.

The magma (mixed), as taken from the sieves, has the following average composition:

Water	62·27
Ash	·27
Oil	1·31
Carbohydrates	28·90
Fibre	1·58
Albuminoids	5·67
	100·00

The above milky fluid, washed from the magma, and collected in tanks underneath the sieves, is now allowed to subside, and the supernatant liquor run off. The residue, washed and agitated with fresh water, is again allowed to settle, and the supernatant liquor again run off. This second washing is found to be necessary, especially in warm weather, as the suspended impure starch is apt to turn sour, which would interfere with subsequent operations. The deposited impure starchy matter is now pumped up in a semi-liquid condition into large vats, called 'separators,' which are generally on the top floor of large factories.

These so-called separators are large wooden vats of a cylindrical form, several feet high, and the diameter of which is about equal to the height, having a series of holes, closed by plugs, in the sides, arranged towards the bottom at equal distances apart (6 to 12 inches). Each vat is provided with a mechanical stirrer and the necessary gearing. In all well-regulated factories there is generally a series of such vats. As soon as the impure starchy matter is pumped into these vats, it is diluted considerably with water, and the stirrers put in motion. A solution of caustic soda at 7–8°Bé. is then very cautiously added until the milky liquid has changed to a greenish-yellow colour. The stirring is then continued for some hours, until a sample taken from the vat in a glass or beaker separates into two layers—the bottom layer, which is dark-coloured, containing the impurities, the upper, which is white, being the starch. In passing, it may be remarked that the nitrogenous matter of Indian corn or maize is of two kinds: one which is dissolved by a solution of caustic alkali, the other, which is precipitated, and is of a dark yellowish-green colour. The separation being complete, the machinery is stopped, and the separated starch and glutinous matter allowed to deposit, whilst the supernatant liquid, containing nitrogenous matter, oil, &c., in solution, is run off.

The deposited starch and glutinous matter is next washed with water and well roused up, allowed to rest for fifteen to twenty minutes to allow the insoluble gluten, &c., to subside, when the first plug is drawn, and the starch remaining in suspension in the water is allowed to flow by means of a properly arranged gutter into vats underneath, then the next plug is drawn, and so on to the last. The plugs are then replaced, the vats again filled with water, and the operation repeated. This, which is called the siphoning process, is generally repeated three times, and the runnings of starch are collected in several separate vats, forming the different grades of starch of the factory.

The deposited matters, nearly exhausted of starch by the above means, are all collected and run over what is called the inclined table, consisting of a series of wide gutters side by side, sixty feet long, with a fall of from three to six inches at the lower end. This deposit is allowed to flow evenly and slowly with a stream of water, the lighter portions running off at the end to waste, whilst the starch settles down in the gutters.

The starch siphonings 1, 2, and 3, and which are collected in different vats, are allowed to repose, and the supernatant liquid run off; clean water is run in, the starch once more well roused up, and, if necessary, the siphoning process repeated. In summer, when the temperature is high, it is necessary during this stage of the process to keep the contents of the vats cool by the addition of large lumps of ice.

These three grades of starch produced as above after being well washed with water are finally roused up and run through a fine sieve of bolting cloth into oblong tanks of wood, called 'settlers,' the cloth retaining any fibre or glutinous impurity, while the finer grains of starch run through with the water. The starch then deposits in these tanks hard and firm on the bottom, whilst the water can be run off clear to the surface of the starch.

The next stage in the process is termed 'boxing,' in which the starch is collected in moulds or oblong boxes having a perforated bottom. A piece of muslin is damped with water, and placed round the sides and on the bottom of these boxes; the hard deposited starch is then dug out of the settlers and firmly packed in these moulds up to the brim. As the moisture drains away the starch subsides in the moulds, and more starch is added until further subsidence ceases. It is then allowed to remain for some hours, when the moist starch, which now contains some 60 p.c. of moisture, is turned out on to a table, and the oblong block cut through into equal and convenient-sized blocks or squares. These pieces or squares are next placed on an absorbent medium or floor, generally made of porous brick covered with a layer of plaster of Paris cement, and heated underneath by means of a series of steam pipes. Here the starch remains for some hours until the moisture it contains is reduced to about 45 p.c. It is then ready for the crushing process. The blocks of starch are placed side by side on a rack or shelves in a kiln, and allowed to remain therein exposed to a heat of 120–130°F. until a yellowish-brown crust forms on the outside, varying in thickness from $\frac{1}{8}$ to $\frac{1}{4}$ inch more or less. They are then taken out, and the crust removed, when the interior appears perfectly white. In this state it is wrapped in paper, and again returned to the kiln, and now exposed to a temperature of 156–176 F. for a period varying from three to fifteen days, or sometimes even longer. During this time the blocks of starch separate up into a series of irregularly shaped rods resembling prisms, more or less, and are technically termed 'crystals.' A high temperature and short period in contact therewith gives small pipe crystals, whilst with a low temperature and longer time the starch is obtained in larger chunks and more irregular.

Starch as it comes from the kilns is practically dry, containing only $\frac{1}{2}$ to 1 p.c. moisture, but on exposure to the air it again takes up moisture, and retains its normal condition, containing from 15 to 18 p.c. water as moisture. As a rule, the loss of starch by this so-called sweet process is about 4 p.c.

As already stated, it is of importance in the early stage of the treatment of the corn to remove as much as possible of the oil and mineral constituents of the grain by steeping, in order that the starch may be rendered as pure as possible, and, as an incidental product, to save all the refuse that can with economy be prevented running to waste. As a rule, however, not more than 13·7 lb. of actual dry refuse matter as cattle food is recovered in the treatment of maize per bushel of 56 lbs., the 56 lbs. of grain being represented as follows:

Starch recovered . . .	28·0 lbs.
Dry refuse as food . .	13·7
Bran (in clearing process) .	0·7
Water in grain . . .	5·6
	48·0
Actual loss . . .	8·0
Total . . .	56·0

The above figures show an actual loss of practically 8 lbs. of the solid constituents of the corn, which may be divided among the various constituents of the maize as follows: The 13·7 lbs. recovered as actual dry food is generally recovered as containing 62–80 p.c. moisture, and sold as such, seldom in a dry state. Taking the analysis already given of this magma as containing 62·27 p.c. water, the above 13·7 lbs. would represent 35 lbs. per bushel of moist refuse recovered from one bushel of maize as pigs' food. The wasted matter may therefore be divided among the constituents as follows, the following table being calculated to 2,775 bushels, at 56 lbs. to the bushel, or 155,400 lbs. of maize, this being the average daily consumption of maize in a well-known starch factory in the United States:—

—		Maize in lbs.	Food per cent.	Food recovered in lbs.	Total loss in lbs.
		2,775 bushels, at 56 lbs. =155,400 lbs., less dirt =2,000 lbs.=153,400 lbs.			
Maize contains:—	p.c.				
Water	10·04	15,401½	62·27	62,510	2,031½
Ash	1·52	2,331½	0·27	300	2,031½
Oil	5·20	7,977	1·31	1,305	6,672
*Carbohydrates . .	70·69	108,438½	28·90	29,045	1,693½
Fibre	2·09	3,206	1·58	1,610	1,596
Albuminoids . .	10·46	16,045½	5·67	5,730	10,315½
Total	100·00	153,400	100·00	100,500	22,308½
*Starch	50·00	77,700	trace	trace	trace

The above table will give some idea of the loss of solid matters, other than starch, in a factory of large dimensions, and which is entirely caused by running away with the waste-water—various valuable by-products which, one would imagine, might easily and profitably be recovered and utilised for many purposes at a small extra cost.

22. *Manufacture of starches for edible purposes.* Alimentary substances may naturally be divided into three well-marked groups—carbohydrates, proteids, and fats; and of these fully two-thirds, or perhaps more, of the food of mankind belongs to the carbohydrate group, of which starch is by far the most important member.

In the raw state, according to Roberts (Digestive Ferments, p. 17), starch is to man an almost indigestible substance, but when previously subjected to the operation of cooking it is digested with great facility. Diastase has, at best, only a comparatively feeble action on the unbroken starch granule, even at the temperature of the body. By the aid of heat and moisture in the process of cooking the starch granule is much more effectively broken up, and in the gelatinised state is very rapidly attacked and digested by the diastatic juices of the body.

In addition to the large quantities of starch consumed in the natural form—as rice, potatoes, bread, &c.—numerous forms of prepared starches are met with in commerce as articles of food. These differ in a most essential degree from wheat and other cereal flours in that they consist almost entirely of absolutely pure starch granules, which very readily gelatinise and become easily assimilated.

In this country large quantities of edible starch are manufactured from maize and rice, whilst in France potatoes are largely employed for the same purpose. The colonies furnish a very large proportion of edible starches, the principal being arrowroot from the West Indies, Natal, India, Fiji, and Queensland.

23. *Cornflour.* Although the manufacture of starch from maize has been practised in this country for the last fifty years, the product therefrom—known under various names, such as Indian cornflour, oswego, maizena—has been used chiefly for edible purposes, whilst most of the starch used for other household as well as manufacturing purposes has been that made from wheat and rice.

The process of manufacture carried on at present is essentially that of Polson (Eng. Pat. 1854, No. 668), although various improvements have been introduced from time to time. By this process the grain is first steeped in water until thoroughly saturated; it is then reduced to a pulp by means of a levigating machine, and passed over a sieve, through which the finer portions are forced by revolving brushes, the coarser matters being returned to the mill to be further levigated and re-sieved.

The separated starchy matter still contains some gluten, fibre, and other matters, which are separated by causing the starchy matter, as it leaves the sieves, to flow with much water over an inclined plane, by which means the heavier starch cells subside, whilst the impurities, being lighter, are carried off at the further extremity of the plane. At suitable intervals narrow pieces of wood are placed across the plane, so as to form a series of dams or weirs, which intercept the starch until it accumulates in sufficient quantities to be removed; the starch thus obtained is dried in the usual manner, crushed into powder, and sent into market as cornflour.

When necessary, or when a finer product is required, the starch, as it leaves the planes, is subjected to the alkali process, so as to dissolve the remaining gluten; then washed and dried as before.

Large quantities of rice starch are treated in a somewhat similar way, and sent out for dietetic purposes, under the name of British cornflour and other fancy names.

24. *Arrowroot starch* or arrowroot is derived from plants of the genus *Maranta*, the most important member of which is *Maranta arundinacea*, a native of the West Indies, and which furnishes most of the genuine West Indian arrowroot. Three other species of *maranta* are also cultivated for the production of starch: *M. nobilis*, *M. Allouyia*, which grow in the West Indies, and *M. ramosissima*, which is a native of the East Indies.

The arrowroot plant is herbaceous, from four to six feet high, and has broad, pointed leaves. The tuberous roots or rhizomes are pointed, covered with scales, and sometimes a foot in length and about the thickness of a finger.

The starch is stored in the rhizomes of the plant, and requires to be extracted and purified to render it fit for market.

The following details of manufacture are taken from a paper by J. W. Macdonald, on 'The Manufacture of Arrowroot Starch in St. Vincent' (S. C. I. 6, 334).

The first part of the manufacturing process is to soak the roots in water, to soften the covering and the adhering earth. They are then stripped of the covering and washed, and thrown into a second or rinsing tank. When thoroughly clean they are taken to the pulping machine. The skin is said to contain a resinous matter, which gives a yellow tinge and unpleasant flavour to the starch if the latter is not well washed. In former times the roots were skinned with German-silver knives before being pulped. This is said to have produced whiter starch; but as it was so laborious and expensive, it was discontinued. The skinned roots were pulped by subjecting them to great pressure by passing them through an upper, and then a lower and much closer, pair of brass rollers, to break the starch cells. The method of pulping now generally adopted is to feed the clean unskinned roots against a fine saw grater very similar to a potato grater. It is a solid cylinder of hard wood, about 23 inches diameter and 7 inches wide. Slits are made by a saw from end to end of the wood at half-inch intervals. Saw blades having six to ten teeth to the inch are then fitted into the slits, and the whole immersed in water to swell the wood and fix the saws. The grater is now fitted into its place very close to a wooden feeding bed. As it revolves several hundred times per minute, it tears the roots into shreds. A great deal, however, depends on the fineness of the teeth and the velocity of the drum.

On account of the very fibrous nature of the pulp, there is considerable difficulty in the sieving or separating of the starch from it. The fibres readily gather into lumps and inclose the starch, so that hand-sieving, although very tedious, has to be resorted to. The pulp is first run into a box or sieve, the bottom of which is a sheet of copper or tin punched with holes one-fifth of an inch diameter. While water flows on, the contents are kept thoroughly agitated by hand until all the starch has been washed out. While one strainerful is being washed, another is being filled, so that there should be no delay. However careful one is, there is a loss of starch in the fibre, owing to the presence of small bits of roots which have escaped pulping.

In one factory a stationary half-cylinder is employed. Its under side is pierced with small holes; but there is a slide under this to open or close at will. Inside there are rakes attached to two shafts, which move in opposite directions and cause the rakes to oscillate very rapidly between each other, thereby keeping the fibre always open. The starch water is let out, more water run in, and the operation repeated until all the starch is extracted, after which the fibre is taken out. The great objection to any mechanical washer is the tendency of the fibre to accumulate on the agitators and break them. To get over this difficulty it has been proposed to chop up or slice the roots into small, short pieces, and either rasp them or pass them through metal rollers or millstones, so that the thin disintegrated pulp may flow over mechanical sieves. Although causing a loss of starch, the present method of rasping avoids an undue pulverising of the soft yellow fibre, and so gives a very white starch without much trouble.

From the fibre-strainers the starch water flows consecutively through a series of brass wire sieves of 40, 80, and 100 meshes to the inch; each of these retain small fleshy bits of unpulped root. From the last sieve the water runs into the settling cisterns, which are preferably lined with white glazed tiles to avoid accumulation of slime.

A portion of fibre collected on the finer sieves is used for feeding the animals on the estate; the remainder, and all the coarse fibre, is used as manure. For this purpose it is left in heaps until it decomposes, after which it is distributed on the fields along with pen manure; sometimes ashes and guano are used. The waste water from washing the starch contains a considerable amount of vegetable matter, and gives good results where it is run on the fields; but the extensive application is not practicable. After the starch has settled in the cisterns the water is run off, and more added; the whole is stirred up again, and allowed to settle. This generally suffices to dissolve out soluble matters. At night all the cisterns are drained, and the starch is dug out and taken to a mixing-box, where it is mixed with a small amount of water, then run through another fine sieve into the separating pans. These are small round galvanised cisterns, with smooth perpendicular sides. When filled, the starch-milk is stirred round with a small oar until it is in violent circulation. The oar is withdrawn, and the cisterns left until morning. The stirring has the effect of separating the starch from any remaining impurities. These, being of less specific gravity, settle last, and therefore on the top of the starch. Next morning the water is drained off, and the light, impure starch scraped off the surface. If the earlier parts of the process are carelessly done, this separation may have to be repeated before the starch is quite pure. The impure surface starch contains a large proportion of starch entangled in very fine particles of fibre and broken cell walls. Although this can be dried and exported as an inferior starch, it is generally given to the labourers as a perquisite. It is used in various forms as flour. Poultry and pigs are also fed with it. Weak caustic soda extracts a colouring matter from it, but also precipitates a yellow substance, making it very difficult to separate the starch from it in a pure state.

The pure starch in the separators is now taken out in blocks, and placed on trays for about twelve hours to dry and harden. It is then broken into smaller pieces and taken to the drying house, where it is air-dried, the building being open on all sides for free circulation. It is surrounded, however, with galvanised wire to keep out the small birds which hover about. Inside there is a series of wire shelves over large shallow wooden trays. The top shelf is made of very open wire, the next is closer, and so on, the lowest being the closest. The wet lumps of starch are placed side by side on the top shelf, where they remain until, by the action of the air, they crack up and fall through to the next shelf. In time the whole falls through the lowest shelf, and is in a fine granular state, ready for packing. It contains from 14 to 17 p.c. of water. In cold, wet weather the starch dries very slowly, taking sometimes as long as two weeks. During this time, if it has been imperfectly purified, the lumps get sour and become yellowish. Indeed, the whole process must be as rapid as possible. In the settling cisterns especially, if the starch is left in contact with the impure water too long, its whiteness is affected. The crop lasts from October to May. The name 'arrowroot' is probably derived from the Indian word Ara-ruta, or 'mealy root'; but some say that this root has been confounded with the *Maranta galanga*, which was called the arrowroot on account of its bruised roots being employed as an antidote to the poison of the *Jatropha Manihot*, used for poisoning arrows.

Regarding the yield of arrowroot, an acre will produce 13,000 to 15,000 lbs. of roots, according to the season; in wet seasons the roots are heavy and moist, and give less starch. A fair average yield is 22 cwts. air-dried starch, with 14 p.c. water, per acre, or about 19 p.c. on good roots. There is no doubt this can be considerably increased by the use of improved pulping and sieving machinery.

The following analyses will give an idea of the constituents of the roots, as well as of the composition of the finished starch:—

—	Roots	Starch
Starch	27·07	83·70
Fibre	2·82	0·04
Fat	0·26	0·07
Albumen . . .	1·56	
Sugar, gum, &c. . .	4·10	0·18
Ash	1·23	0·14
Water	62·96	15·87
	100·00	100·00

The ash consisted of phosphate of lime and alkaline sulphates and chlorides.

Arrowroot swells much more readily and with less heat than maize, rice, or wheat starch, and forms a stiffer jelly. It is, therefore, well adapted for sizing and laundry purposes. As an article of food it must be regarded as the purest, most digestible, and palatable of the starches.

Methods similar to the above are employed for the extraction of arrowroot starch in the East Indies, Natal, and Queensland.

25. *Cassava starch* or *Brazilian arrowroot*. The root which produces this starch is somewhat similar to that of the *Maranta*, and is known as Cassava or Manioc. It belongs to the genus Manihot, the most important of which is *Jatropha Manihot* or *Manihot utilissima*, a native of Brazil, but now cultivated in India, Guiana, West Indies, and various parts of Africa. In Brazil considerable attention has been given to the manufacture of starch from various tubers and roots; but cassava starch is the principal kind which is manufactured there, and is known as Brazilian arrowroot. Its mode of preparation is very similar to that of East Indian arrowroot.

Tapioca is prepared by heating the cassava starch whilst still moist upon hot plates, keeping it well stirred with an iron rod all the time. A large number of the starch granules burst during the process of heating, and adhere together in small irregular masses, in which form it is imported into this country. Tapioca is partially soluble in cold water, and readily swells up in boiling water, forming a transparent jelly.

The natives of Brazil prepare cassava meal by reducing the tuberous roots to a pulp either by rasping or grinding, after having first washed and peeled them. This pulp is then placed in bags made of plaited reeds, and subjected to pressure, so as to express the juice. The residue —consisting of a mixture of starch, vegetable fibre, and albuminous matter—is partially dried in the sun and partially on hot plates over a slow fire, and kept continually stirred with a wooden spoon until it is dry, but not browned; it is then known as cassava meal, and used for making bread. The juice is allowed to stand for some time, when the starch contained in it subsides, and is washed with water, constituting a finer meal. The roots of the species known as bitter cassava contain an acrid poison, hydrocyanic acid, which, being volatile, is readily dissipated by heat, or may be washed away with water.

26. *Curcuma starch.* In the East Indies a starch is prepared from the tuberous root of *Curcuma angustifolia*, which is sometimes known as East India arrowroot, and said to be rather extensively manufactured in Travancore and other parts of North-west India.

27. *Arum starch.* A starch very much resembling cassava starch, and which was used as a substitute for arrowroot, and known in the market as Portland arrowroot, was obtained from the roots of the wild arum, or *Arum maculatum*, this plant being formerly cultivated in the Island of Portland for this purpose.

28. *Tous-les-mois.* This starch, the granules of which are the largest known, is extracted from the rhizomes of the *Canna edulis*, a native of the West Indies, principally at St. Kitts. That which is imported into this country is used partly in the manufacture of cocoa and partly in the preparation of food for infants.

29. *Sago.* This is the name given in commerce to a prepared starch obtained from the pith of several varieties of palms, which are indigenous to the Malayan archipelago, the Philippine Islands, and parts of India. Wherever there is a soil suitable for their cultivation, this consists of marsh or bog land, composed of decayed vegetables, near the sea. The principal species are the following: *Sagus Rumphii*, *Sagus farinifera*, *Borassus flabelliformis*, and *Arenga saccharifera.*

All these palms propagate themselves by lateral shoots as well as by seed, so that a sago plantation, when once formed, may be said to be perpetual. The growth is slow at first, but when once fairly started proceeds rapidly, until a height of some 20 to 30 feet is attained by the stem.

The sago tree, when cut down and the top severed from it, represents a cylinder about 20 inches in diameter, and from 15 to 20 feet in length, consisting essentially of a hard woody tube, the interior of which is filled with starch granules intermixed with fibrous matter. From such a tree about 700 lbs. of starch would be extracted, so that three such trees would yield nearly double as much food material as one acre of wheat. Sago is, however, far from being either so palatable or nutritious as it is prolific, and even where it is more abundant is never preferred to rice.

By far the greater portion of sago imported into this country comes in the raw state as sago flour, and is used to a very large extent in the manufacture of glucose. Singapore is the headquarters for exportation of sago, both raw and manufactured being brought there from the islands to the eastward, principally from the north-west coast of Borneo and the north-east of Sumatra, with its adjacent isles from Siak to Indragari, as well as from many other places more distant.

To obtain the starch or flour, the trees, as soon as they have arrived at a suitable stage of growth, are cut down close to the roots, the stems sawn into pieces 7 or 8 feet long, which are split open and the pith extracted. This is then pounded up in wooden mortars so as to reduce it to powder, agitated with water in a trough, run through sieves to free the starch from cellular tissue and fibrous matter, allowed to settle, and, after washing several times with water, is dried and sold as sago flour.

What is known as granulated or pearl sago is prepared from sago flour in the following manner:—The flour is made into a stiff paste with water, and rubbed through a metal sieve into a heated, very shallow, copper or iron pan, greased inside with vegetable fat. During the process of heating, the starch granules are kept constantly agitated, a portion of them swelling and becoming pasty serve to bind the remainder of the granules together. The resulting cohering particles obtained in this way are called pearl sago, of which two kinds are known in commerce, one consisting of small grains about the size of rape seed, and the other of grains about twice or three times the size.

Granulated sago appears to have been introduced into Europe in the early part of the eighteenth century, but there is reason to believe that the starch from the sago palm has been used as an article of food by the natives of those countries in which it grows from a very remote period.

A sample of pearl sago gave on analysis:

Starch	84·64
Water	15·22
Mineral matter . . .	0·14
Total . . .	100·00

In recent times, in Germany and France, sago has been made from potato starch, and introduced into commerce as 'Indian sago,' the best specimens of these imitations surpassing real sago in appearance and whiteness; so that the question arises, Is there any essential difference between the European imitation and the real sago of the tropics? Opinions as to goodness of flavour differ, and in reference to the nutritive values of the two there have been no scientific investigations. *A priori*, it is not impossible that the nutrient value of the real is greater than that of the artificial, since the former contains more granulose. However, the difference between the relative values of the two is not nearly so great as the difference in price, which stands almost as 1 : 2.

Sago has the property of swelling up in hot fluids without losing its coherence; the granules do not fall to pieces, but appear as transparent and gelatinous, but not sticky, spheroids.

30. *Inulin.* In the tubers of the dahlia, Jerusalem artichoke, and other plants of a similar character, there occurs an amylaceous substance which bears a very close resemblance to starch, having identically the same ultimate composition, and which, indeed, for all practical purposes may be regarded as another form of starch. To this substance the name of *inulin* has been given.

Kiliani (A. 205, 145) prepares inulin as follows. Roots of *Dahlia variabilis* are well washed, and, after being rasped, are boiled with water in the presence of sodium carbonate. The liquid obtained is cooled by means of a freezing mixture, allowed to stand some time, and the precipitate which settles out dissolved in hot water, filtered whilst hot, and again exposed to a freezing mixture. This process is repeated three or four times, after which the inulin is obtained as a perfectly white substance. It is then treated with alcohol, whereby any levulose that may be present is removed, and the inulin finally dried over sulphuric acid *in vacuo.*

Inulin is not acted upon by diastase, but is converted into levulose when heated with dilute acids.

31. *Lichen starch.* In Iceland moss there occurs a form of starch easily soluble in water, from which it is thrown down as a flocculent precipitate by alcohol, and which gives the characteristic blue colouration with iodine. It rotates polarised light strongly to the right, and is readily converted by diastase into dextrin and maltose. Lichen starch, therefore, appears to be a soluble, unorganised modification of ordinary starch.

32. *Glycogen.* In the livers of most animals there is produced a white amorphous substance which forms an opalescent solution with water, from which it is precipitated by alcohol, and is transformed into dextrin and maltose by the action of diastase, and to which the name of glycogen has been given. It may be regarded in every sense as an exact counterpart of soluble starch, and is considered to be reserve starch material elaborated from the sugars and other carbohydrates consumed as food.

33. *Detection of starch.* The presence of starch existing in the solid state in any substance is most readily detected by microscopic examination, supplemented, where necessary, by the addition of iodine solution to the slide, when the characteristic blue colouration is at once observed if any starch granules are present. In this way the presence of starch in chlorophyll granules may be readily detected by Sachs' method (C. C. 1884, 945). The fresh green leaves are plunged into boiling water for ten minutes; certain soluble substances are thereby extracted, whilst the starch and colouring matter of the chlorophyll grains remain intact. A short immersion in 96 p.c. alcohol now removes the green colouring matter and certain bodies soluble in alcohol, leaving the starch behind in the colourless tissue, the decolouration proceeding more rapidly in sunlight or warm alcohol than in the dark and cold. After this treatment the leaves are placed in a strong solution of iodine, made by dissolving iodine in alcohol, and then diluting with distilled water until the liquid has a dark-brown colour. They are allowed to remain in this liquid for about an hour, or until they no longer acquire colour. If no starch is present the leaves are simply stained yellow; if they are stained slightly black, very little starch is present. If a large quantity of starch exists in the cells, the tissue appears blue-black or black, with a metallic lustre, the venation appearing as a pale network in the dark ground. By this means the absence of starch from etiolated leaves, from the white portions of variegated foliage, and from those portions of the leaf which have been covered by paper or tinfoil, may be readily demonstrated.

When a sample of a substance supposed to contain starch is to be examined under the microscope, it is first reduced to a fine powder, if not already in that state; a small quantity of it is then mixed up with some water in a watch-glass by means of a glass rod, and a drop of the mixture placed on the slide, a cover glass put on, any superfluous moisture round the edges of the cover-glass carefully removed with blotting-paper, and the slide next placed under the microscope; the stage should be illuminated with rather oblique light, a $\frac{1}{4}$ or $\frac{1}{5}$ inch objective, with a B-eye piece, being the most suitable magnifying power to employ.

The following points should be observed: the size and form of the granules, the position and character of the hilum, the nature of the striæ or concentric rings, and the appearance presented by the granules under polarised light. In the latter case, it is advisable to mount the sample in glycerin instead of in water; a red-green selenite plate may also be advantageously employed. It is only by careful microscopical examination that one particular form of starch can be differentiated from another, and it is comparatively easy when only one kind of starch is present; but when mixtures of different starches occur in the same sample, the detection of each particular one becomes a matter of some difficulty.

The following method, as given by Bell (Chemistry of Foods, 2, 151), appears to be practicable for most of the commonly occurring varieties:

To insure the homogeneousness of the sample, it is first rubbed in a mortar, and passed several times through a sieve. A small quantity, say 0·5 of a grain, is then weighed out and placed upon a glass slide, where it is worked into a thin paste with about two drops of water. A thin covering-glass, measuring about 1$\frac{1}{2}$ inch by 1 inch, is then placed over the paste, and moved about the slide until the paste is equally distributed and all under the covering-glass. With a $\frac{1}{4}$-inch objective and B-eyepiece the number of granules of foreign starch is counted in nine 'fields,' as fairly as possible representing the entire slide. The pro-

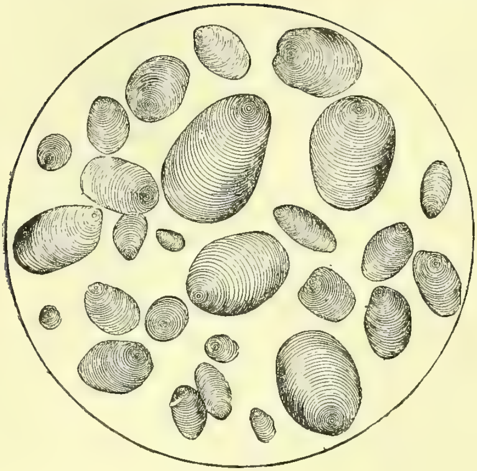


FIG. 15.

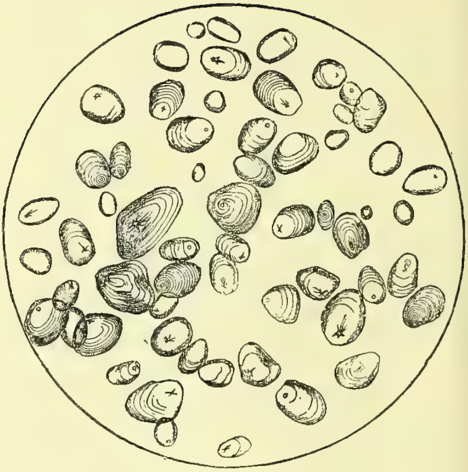


FIG. 16.

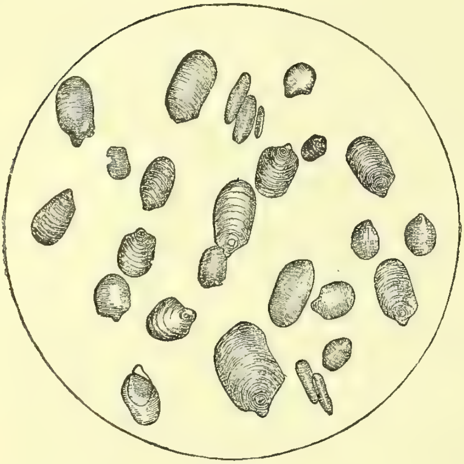


FIG. 17.

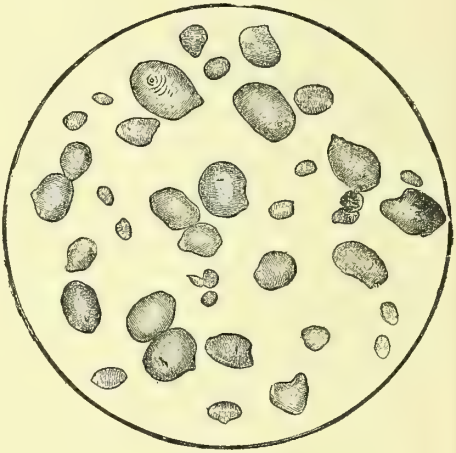


FIG. 18.

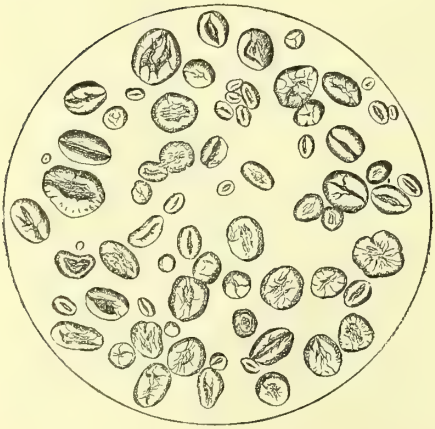


FIG. 19.

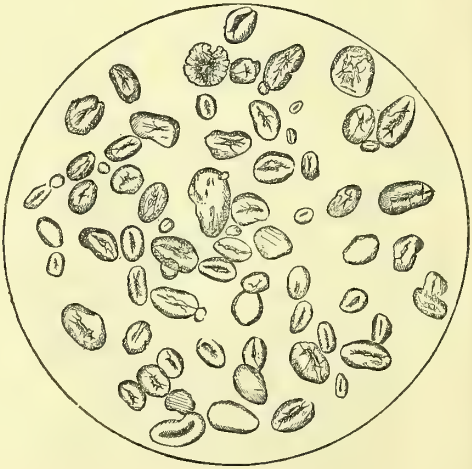


FIG. 20.

cess is repeated until a correct idea of the composition of the sample is obtained.

Standard mixtures approximately representing the sample are then made up and treated in exactly the same way, and, from a comparison of the results, the percentage of foreign starch is computed.

When the percentage of foreign starch is large it is advantageous, in order to facilitate the counting of the granules, to insert in the eyepiece a slide accurately divided into squares.

In cases where the granules of added starch are so small and numerous that it is impossible to count them, as with rice starch, a similar process of preparing the slides is followed, and as correct an estimate of the foreign starch is made as is possible by a comparison of the appearance of the sample with that of the standard mixtures.

It is often advisable to use a dilute solution of iodine instead of water in preparing the slides for examination, as the resulting colouration of the starch granules renders them more distinctly visible.

As an aid to their microscopical examination and recognition, Allen (Commercial Organic Analysis, 335), following Muter, arranges the starches into five classes, having the following general characteristics:—

I. The Potato Group includes such oval or ovate starches as give a play of colour when examined by polarised light and selenite plate, and having the hilum and concentric rings clearly visible.

II. The Leguminous Starches comprise such round or oval starches as give little or no colour with polarised light, have concentric rings all but invisible, though becoming apparent, in many cases, on treating the starch with chromic acid, while the hilum is well marked, and cracked or stellate.[1]

III. The Wheat Group comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes starches from wheat and some other cereals, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, &c.[2]

IV. The Sago Group comprises those starches of which all the granules are truncated at one end. It includes some starches used for food, together with those from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.

V. The Rice Group contains the starches, all the granules of which are polygonal in form. It includes the starches from oats, buckwheat, rice, pepper, and ipecacuanha.

34. *Microscopical appearance of different varieties of starch.* The microscopical appearance of the different varieties of starch granules is shown in the following illustrations, which are taken from Dr. Bell's Chemistry of Foods, Pt. II., by the kind permission of the author.

Class I.—(*a*) *Canna*, or *Tous les mois* (fig. 15). The granules of this starch are the largest known, are ovate in form, rounded at one end, and more or less pointed at the other, near which is situated the circular hilum. The rings are well marked, but not complete.

(*b*) *Potato* (fig. 16). Granules vary much in form, the smaller ones being more or less spherical, whilst the larger are ovate or oyster-shaped. The hilum, which may be circular or stellate, is generally near the smaller end. In the larger granules the concentric rings are very distinct and complete.

(*c*) *Maranta* or *arrowroot*. According to Bell, *Bermuda arrowroot* (fig. 17) may be taken as the most perfect type of a maranta starch. In no other kind of arrowroot do the granules so generally exhibit an irregularly oval form, with the peculiar, small, nipple-like projection near one end, and where also is situated the hilum, which is either circular or linear. The rings are concentric and numerous, always visible, but not strongly marked.

(*d*) *Natal arrowroot* (fig. 18), as compared with Bermuda, may be taken as an example of the divergence which occurs in the form, size, and general appearance of the starch granules yielded by different varieties of maranta. The hilum is generally linear. The rings are very distinct under water.

Class II.—*Bean*, *Pea*, and *Lentil* (figs. 19, 20). These starches are very similar in appearance, and not distinguishable from one another in mixtures. The granules are oblong, kidney-shaped, and irregularly formed, most of them having a longitudinal cavity running along each granule lengthwise, and from which, in many instances, furrows diverge to the right and left, imparting to their surfaces a fractured appearance.

Class III.—*Wheat* (fig. 21). The granules, which are nearly circular, present a flattened appearance under the microscope, and are generally of two sizes—large and small. Hilum central; rings concentric and very faintly marked.

Barley (fig. 22). The granules are very similar to those of wheat, but rather more irregular in shape.

Rye (fig. 23). The granules of this starch are larger than those of wheat or barley, are more circular in form, and present a flattened appearance and fractured surface. The hilum in the majority of the granules is stellate.

Class IV.—*Sago* (fig. 24). The granules are elongated, rounded at one end and truncated at the other. Hilum circular, stellate, or linear, near convex end. The rings are concentric, numerous, and but faintly visible.

Cassava (fig. 25). The granules are similar to those of sago, but not so elongated, presenting more the appearance of a kettledrum. The hilum, which is well defined, is situated near the centre.

Arum (fig. 26). Somewhat like cassava, but much smaller.

Class V.—*Rice* (fig. 27). The granules of this starch are the smallest of all the commercial starches, and are pentagonal or hexagonal in form. Hilum extremely minute, but distinct with a very high power.

Maize (fig. 28). The granules are polygonal, but approaching to circular, and are intermediate in size and general appearance between the starch

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[1] All these starches present very close resemblances, and are generally indistinguishable from each other when in admixture.

[2] The cereal starches may be divided into two well-defined groups, wheat, barley, and rye starches being circular, or nearly so, while the starches of rice, maize, buckwheat, and oat are polygonal.

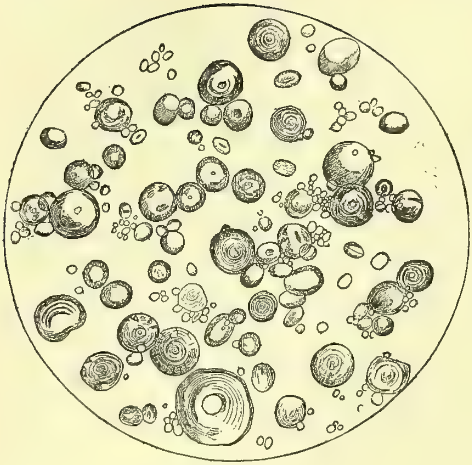


Fig. 21.

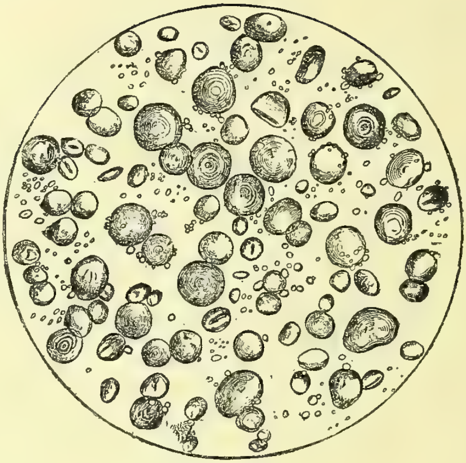
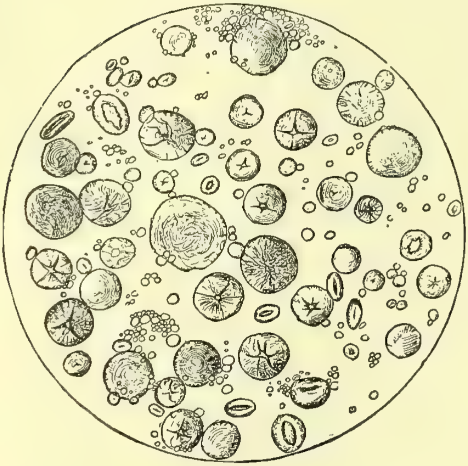


Fig. 22.



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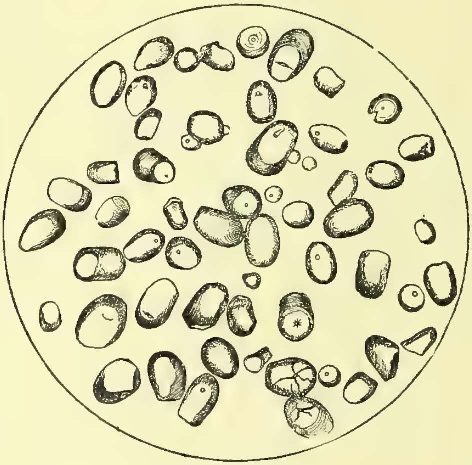

Fig. 24.

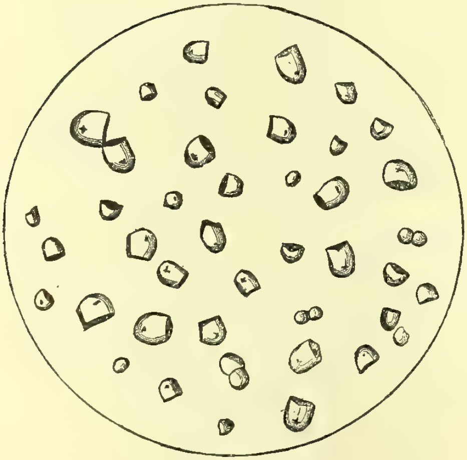

Fig. 25.

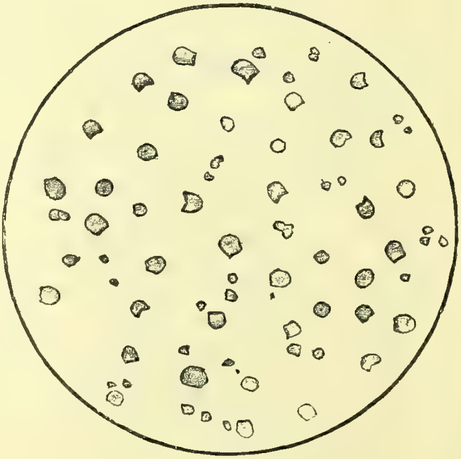

Fig. 26.

granules of wheat and oats. The hilum is central and stellate.

Oat (fig. 29). The granules are triangular to hexagonal in form. Both rings and hilum are invisible except under very high powers.

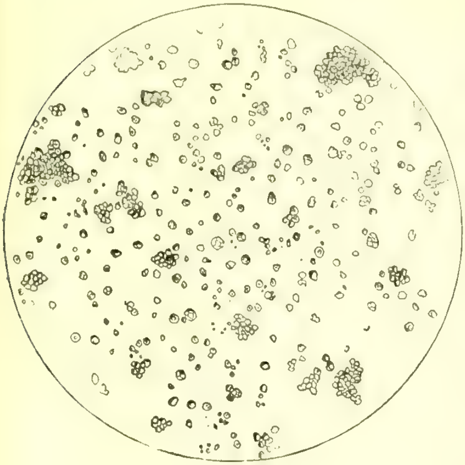

Fig. 27.

For illustrations of various other forms of starch granules, see under 'Starch' in Payen's Chimie Industrielle.

35. *Estimation of starch.* Various methods have been proposed and described for the determination of starch in different substances, both as raw materials and products of manufacture. As the conditions under which starch occurs in such substances vary so much, it naturally follows that one and the same method cannot be applied for its estimation in all cases, but the same general principle applies to all—viz. the extraction of the starch, either in a state of purity or after its decomposition into dextrin and maltose, or into dextrin, maltose, and dextrose, then estimating the amount of these starch products by one of the methods given under *Saccharimetry*, art. Sugar.

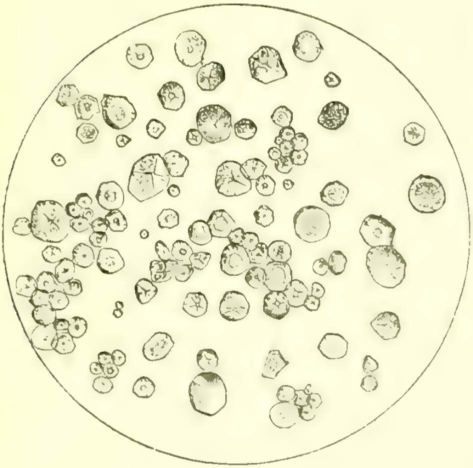

Fig. 28.

Several methods have been proposed for the direct estimation of starch—such as precipitation with solution of iodine, barium hydroxide—but none of these methods can be said to have yielded, up to the present, sufficiently reliable results, and the method of indirect estimation must be regarded as the only one approaching to accuracy. According to this, the starch in the substance under examination is brought into a state of solution, either as soluble starch, or as dextrin and cupric reducing sugars, by heating the substance for a certain time with glycerin, acid or diastase solution, and after filtration either carrying the process of decomposition further, or estimating the starch products first formed.

The most general process employed for the estimation of starch consists in the conversion of starch into dextrose by boiling with dilute acid (2 p.c. or more) for some hours, either with or without pressure, and estimating the dextrose by means of Fehling's solution. This process, even when most carefully conducted, is incapable of yielding anything like accurate results, these invariably coming out too low; on the one hand from the incomplete conversion to dextrose, on the other through over conversion, giving rise to condensation products having a much less or no cupric-reducing power.

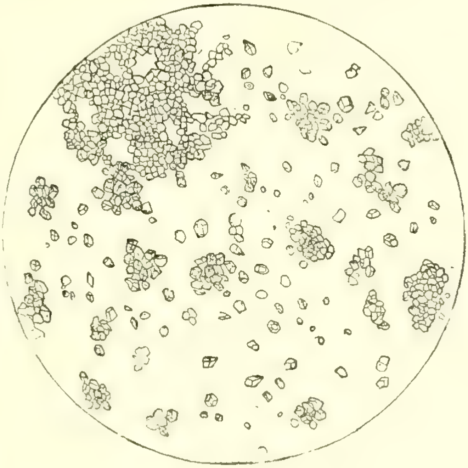

Fig. 29.

A method giving fairly good results is obtained by boiling the starch with dilute acid for about half an hour to one hour, or until iodine solution shows the disappearance of starch, and then estimating the products of decomposition.

Twenty-five grms. of the substance are placed in a beaker, and heated on the water-bath with about 200 c.c. water containing 2 c.c. of strong hydrochloric acid, stirring occasionally for about one hour. The solution is then cooled down to the normal temperature, transferred to a 250 c.c. flask, the beaker washed out two or three times with water, and the washings added to the liquid in the flask until it is made up to the containing mark at 15·5 C. The whole is then well shaken and filtered, and the sp.gr. taken. The same quantity of acid as was taken for the conversion is introduced into a 250 c.c. flask, and diluted with water to the containing mark, the sp.gr. of this deducted from the sp.gr. of the starch conversion gives the sp.gr. due to the starch products, the resulting dextrin, maltose, and dextrose being estimated in the usual way.[1]

Where the starch, either as raw material or as a manufactured product, is required for the purpose of making glucose, it is often for technical purposes sufficiently accurate to heat the substance under examination with acid as above, but for three hours, using an inverted condenser, and estimate the starch products or yield of extract from the sp.gr. only of the solution.

Hönig (Chem. Zeit. 14, 868) describes a method for the estimation of crude fibre and starch based upon the action of boiling glycerin upon starch which appears to the writer to offer a ready means for the determination of starch in potatoes and other tubers, roots, and fibrous substances.

The finely-pulverised (or grated) material is placed in a test tube along with some glycerin, and supported in a bath of concentrated sulphuric acid or some other suitable liquid which can be raised to a high temperature, and then gradually heated to 210°C., for about half to three quarters of an hour. The tube is then taken out of the bath, cooled to 130°, the contents poured into 95 p.c. alcohol, the tube rinsed out with a little water, and ether added. The precipitated soluble starch is washed with a mixture of alcohol and ether (5 : 1), drained, and boiled with water containing 2 p.c. hydrochloric acid for half an hour. The starch dissolves, and is filtered from the cellulose, further inverted, and the starch products estimated in the usual way.

Or the precipitated soluble starch may be dissolved in water, boiled until the alcohol is all expelled, cooled down to 65°C., treated with diastase, and the dextrin and maltose determined.

For the estimation of starch in all the cereals, raw as well as malted, the method recommended by O'Sullivan (C. J. 45, 1) is undoubtedly the best and most reliable, and is carried out in the following manner:—

A fair sample of the grain is taken, and of this 5·1 grms. are weighed roughly, and ground fine in a coffee-mill, kept clean for the purpose. Of the finely-ground flour, 5 grms. or thereabouts, accurately weighed, are introduced into a wide-necked flask, capable of holding 100 to 120 c.c. The flour is just saturated with alcohol, sp.gr. 0·82, and then 20 to 25 c.c. ether added. The flask is corked and put aside for a few hours, the deposit being shaken occasionally. The clear ethereal solution is decanted through a filter, and the residue washed by decantation with three or four fresh quantities of ether, the washings being passed through the filter. To the residue 80 to 90 c.c. alcohol, sp.gr. 0·90, are added, and the mixture kept at 35–38° for a few hours, with occasional shaking. The alcoholic solution, when clear, is decanted through the filter used in filtering the ether solution, and the residue washed a few times by decantation with alcohol, of the strength and at the temperature indicated. The residue in the flask, and any little that may have been decanted on the filter, is then washed with water into a beaker capable of holding half a litre, and the beaker nearly filled with water. In about 24 hours the supernatant liquid becomes clear, when it can be gradually decanted through a filter. The solution filters bright, but in the case of barley and oats exceedingly slowly at times; the malted grains, as well as wheat, rye, maize, and rice, yield solutions requiring no excessive time to filter. The residue is repeatedly washed with water at 35–38°, but even this treatment does not completely free barley and oats from *a*-amylan, which dissolves with the greatest difficulty at this temperature. The residue is then transferred to a 100 c.c. beaker, and the portion adhering to the filter washed by opening the filter paper on a glass plate, and removing every particle by means of a camel's-hair brush, cut short, and a fine-spouted washbottle. When the transference is completed, the beaker, which should not now contain more than 40 to 45 c.c. of liquid, is boiled for a few minutes in the water-bath, care being taken to stir well when the starch is gelatinising, to prevent 'balling' or unequal gelatinisation. After this the beaker, still in the bath, is cooled to 62–63°, and 0·025 to 0·35 grm. diastase, dissolved in a few c.c. of water, added. A trace of the solution ceases in a short time to give a blue colour with iodine, the starch being completely decomposed and dissolved. Yet it is well to continue the digestion at 62–63° for an hour, as the solution, as a rule, filters better. At the end of that time the contents of the beaker are boiled for eight or ten minutes, thrown on to a filter, and the filtrate received in a 100 c.c. measuring flask. The residue is carefully washed with small quantities of boiling water at a time. When the flask is nearly full its contents are cooled down to 15·5°, and made up to 100 c.c. with water at that temperature. If care be not taken to put on small portions of water at a time during the washing, the filtrate may exceed 100 c.c. before the residue is perfectly free from soluble matter; in this case the solution must be evaporated to less than 100 c.c., and then made up to that bulk after cooling to 15·5°.

Treatment with ether frees the grain from fat, &c., alcohol of 0·90 removes the sugars, the albuminoids other than casein, &c., and water at 35–38° is intended to dissolve the amylans, &c., whilst the diastase is made to act on the residue at the temperature and under the conditions that it dissolves starch. The 100 c.c. solution contains, therefore, the products of the transformation or decomposition of the substance.

For manufacturing purposes, however, the mere determination of the total amount of starch in a sample of grain is of little value, as no distinction is made between the insoluble and soluble starch, as the latter is useless if the grain is to be used for making starch. Also the amount of gluten seriously affects the quantity of starch obtainable from the grain, for which allowance must be made in valuing the sample. According to Schreib (Z. 1888, 24), each part of gluten in rice causes the loss of an equal quantity of starch in the course of manufacture; consequently, a sample of rice containing 78 p.c. of starch and 4 p.c. of gluten would be more valuable than a sample containing 80 p.c. of starch and 8 p.c. of gluten, as 74 p.c. of starch could be obtained from the former, and only 72 p.c. from the latter (the yield being found by deducting the percentage of gluten from the total starch in the sample). In the case of wheat the gluten is a valuable by-product, but in rice it is so difficult to separate from the starch—and when separated can only be sold for cattle-feeding or manurial purposes—that the less gluten the rice contains the more valuable it is. Schreib prefers, in making an analysis of 'broken rice,' to estimate the gluten, ash, and moisture, and determine the starch by difference, after making a fixed allowance for the other non-starchy constituents of the grain—that is, fat, sugar, gum, and cellulose. The whole analysis by this method can be finished in four hours, or considerably less time than is required for a direct estimation of the starch by the methods already given.

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[1] This method always gives results which are too high, due to a small portion of cellulose becoming converted during the digestion with acid, but as this also happens in the manufacturing process a fair idea may be obtained of the quantity of commercial glucose obtainable.

Several varieties of starch are largely used in the adulteration of cocoa and chocolate, sago being frequently used for this purpose; but, owing to the variable amount of starch in cocoa beans, a chemical analysis of the supposed adulterated article cannot be regarded as decisive, unless the percentage of starch found amounts to more than 10 p.c. In such cases it is advisable to resort to microscopical examination, and for this purpose the chocolate is best deprived of its fat and sugar before being placed under the microscope. The following method of examination is recommended by Hartwich (Chem. Zeit. 12, 375). The number of starch granules (which may be stained with iodine solution if advisable) in each field is counted, and a mean taken; a pure chocolate is then mixed with a corresponding amount of the supposed foreign starch, and examined in the same manner. In this way the quantity of starch added as an adulterant may be estimated with sufficient accuracy.

For estimation of starch in fodder, Leclerc (J. Ph. [5] 21, 641) gives the following method: 5 grms. of straw, hay, &c., are placed in a 250 c.c. flask, 10 c.c. of water added, and shaken about until every particle of the substance under examination is thoroughly moistened. 180 c.c. of a neutral zinc chloride solution, sp.gr. 1·450, are next added, and the whole heated in a salt-water bath at 108°C. for $1\frac{1}{2}$ hours. The flask is then taken out and cooled down, and the volume made up with zinc chloride solution to 253 c.c. at normal temperature and filtered. From 25 c.c. to 100 c.c. of the filtrate is poured into a beaker containing 2 c.c. to 8 c.c. of hydrochloric acid and a sufficient quantity of 95 p.c. alcohol added to precipitate the whole of the dextrin and starch. After twenty-four hours the precipitate is collected on a tared filter and washed with 90 p.c. alcohol containing ·5 p.c. hydrochloric acid until free from zinc chloride. The acid is then washed out with alcohol alone, and the precipitate weighed, then burnt, and the weight of the ash, of which there is usually a little, being carried down by the alcohol with the starch, deducted.

Starch is of very general occurrence in paper, and may be very easily detected by moistening the latter with a dilute solution of iodine, the intensity of the violet to blue colouration often forming the only means employed to ascertain the quantity of starch present. For the quantitative estimation of it Würster (D. P. J. 229, 538) proceeds as follows. The quantity of water present is first estimated, then the resin, by boiling out with alcohol, drying the paper, and weighing. The starch is next dissolved out by boiling the paper for some time with a mixture of equal parts of water and alcohol, to which a few drops of hydrochloric acid are added, and drying and weighing the residual paper; but, since the acid causes a certain loss in mineral constituents, the ash must be determined in the paper before and after extraction, and the difference deducted from the result. The following p.c. results were obtained on analysis by this method:—

Paper	Water	Resin	Starch	Ash	Fibre and cellulose by difference
Fine post, thin . . .	7·2	2·9	3·5	1·8	84·6
Fine post, medium . . .	7·6	5·4	3·1	1·9	82·0
Fine post, strong . . .	7·2	3·4	3·7	7·8	77·9
Common writing paper . .	5·8	3·9	9·1	33·4	47·8

The starch met with in commerce and used for laundry and manufacturing purposes is almost exclusively derived from rice, maize, and potatoes, and generally contains very little or no impurities. These, when they do occur, consist of vegetable fibre, gluten, or albuminoid matter, remains of pulp water, and other mineral matters. Fibre gets into the finished starch owing to imperfect arrangement of the sieves. Remains of pulp water in starch are owing to bad washing, whilst the presence of sand and other mineral matter may be due to the mixing of that portion of the starch which settles in the washing tanks next to the axis of the stirring apparatus, with the bulk of the starch—or to addition as an adulterant.

The quantity of mineral matter in starch should not exceed 0·5 p.c. When it is more than this, mineral matter, frequently barium or calcium sulphate, has been added; or the starch has been carelessly washed and not properly purified—in this case the other impurities will also be high.

As has already been stated, the proportion of moisture in ordinary air-dried starch averages about 18 p.c. It may be determined by drying the starch *in vacuo* over sulphuric acid, and finishing off in a current of dry air at 100°C., the temperature being very gradually raised to this point. If the starch is at all acid, this must be neutralised by moistening it with a few drops of very dilute ammonia.

For the estimation of water in potato starch, Saare (Chem. Zeit. 52, 934) has worked out a method which combines rapidity of execution with sufficient accuracy for technical purposes. 100 grms. of the starch are rinsed into a tared 250 c.c. flask, which is then filled up to the mark with water at 17·5°C. and weighed; the weight of the empty flask is now deducted from this, and the percentage of water corresponding to the difference found from the following table:—

Weight found	Water p.c.	Weight found	Water p.c.
289·40	0	277·20	31
289·00	1	276·80	32
288·60	2	276·40	33
288·20	3	276·00	34
287·80	4	275·60	35
287·40	5	275·20	36
287·05	6	274·80	37
286·65	7	274·40	38
286·25	8	274·05	39
285·85	9	273·65	40
285·45	10	273·25	41
285·05	11	272·85	42
284·65	12	272·45	43
284·25	13	272·05	44
283·90	14	271·70	45
283·50	15	271·30	46
283·10	16	270·90	47
282·70	17	270·50	48
282·30	18	270·10	49
281·90	19	269·70	50
281·50	20	269·30	51
281·10	21	268·90	52
280·75	22	268·50	53
280·35	23	268·10	54
279·95	24	267·75	55
279·55	25	267·35	56
279·15	26	266·95	57
278·75	27	266·55	58
278·35	28	266·15	59
278·00	29	265·75	60
277·60	30		

The results obtained are correct to 0·5 p.c. The method may also be applied to the estimation of the water in 'green' starch, and may be used for testing the progress of the drying process in the drying chambers. J. H.

STAR SAPPHIRE *v.* CORUNDUM.

STEAM. Steam is water changed from a liquid to an aeriform state, or water vaporised by the agency of heat. By English engineers one unit of heat is the amount required to raise 1 lb. of water from 32° to 33°F.; practically every addition of 1 unit of heat to 1 lb. water in an open vessel increases the temperature of the water by 1°, up to the boiling-point, 212°F. The addition of heat after that does not increase the temperature, but converts the water, or a portion of it, into steam.

The quantity of heat required to convert 1 lb. of water into steam, from an open vessel, or at atmospheric pressure, is 1146·1 units, as given in the third column of the table (p. 596) of the properties of saturated steam.

In a closed vessel, such as a steam boiler, the temperature at which steam is produced differs with different pressures (see Table, p. 596). The total quantity of heat required to convert 1 lb. of water into steam is very nearly the same at all pressures (see Table).

Let A be the cylinder of a steam engine, and *b* the piston, and let the piston occupy the dotted position *c*. Now let steam at 40 lbs. pressure per square inch above the atmosphere, or 54·7 lbs. absolute (40 + 14·7), be admitted behind the piston, and let the admission be continued till the piston arrives at *d*; then let the steam supply be stopped. The piston can then make no further movement except by virtue of the expansive force of the steam. Assume the piston to have moved to the position *b*, or four times as far from the end of the cylinder as the point *d*, where the steam supply was stopped; the steam in the cylinder will then have been expanded to four times its former volume.

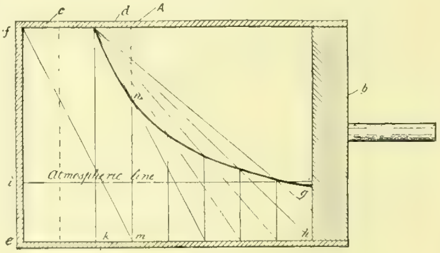


FIG. 1.

Now if we select a scale on which the height from *e* to *f* represents 54·7 lbs., and make *e*, *i* equal to 14·7 lbs., we shall then be able to complete the figure *e*, *f*, *d*, *g*, *h*, *e*, the area of which represents the total force exerted by the steam on the piston, the ordinates of the curve representing on the scale the pressures at the different points occupied by the piston in its movement.

Assuming the cylinder and piston to be perfect non-conductors of heat, the expansion of the steam in the cylinder would follow Boyle's law for the expansion of a perfect gas—viz. that the pressure varies inversely as the volume. We have assumed the steam to have now expanded to four times its former volume; its pressure will then be $\frac{54·7}{4} = 13·67$ lbs.

To find the pressure at any point between *d* and *g*, draw the line *k*, *d*, parallel to *e*, *f* and perpendicular to *e*, *h*; then take any point *m*, making *m*, *n* parallel to *k*, *d*; join *f*, *m*, and draw *d*, *n* parallel to *f*, *m*. The point *n* is a point in the curve of pressures, and *m*, *n* represents on the scale the pressure of the steam when the piston was at that point. All other points in the curve *d*, *n*, *g* can be determined in the same way.

The average pressure of the steam diagram, *e*, *f*, *d*, *g*, *h*, *e* may be calculated thus:

Let R = the ratio of expansion; H, the hyperbolic log. of the number expressing that ratio; P, the initial pressure of the steam; *p*, the mean pressure—then

$$p = \text{P}\,\frac{1 + \text{H}}{\text{R}}.$$

Taking the example before us

$$R = 4, \quad H = 1{\cdot}386, \quad P = 51{\cdot}7;$$

then $51{\cdot}7\,\frac{1+1{\cdot}386}{4} = 32{\cdot}6$ lbs. mean pressure.

We have assumed that the pressure of steam has been fully utilised down to the line *e*, *h*, or line of no pressure or perfect vacuum. In practice this is not realised, and the bottom line of the actual steam diagram is generally 2 lbs. above that of a perfect vacuum; the real mean pressure would therefore be not 32·6 lbs., but 30·6 lbs. We have assumed the steam-engine cylinder to be a perfect non-conductor of heat. It is not so, and the practical effect of its conducting power is, that during the former part of the stroke of the piston, steam is being condensed in the cylinder, and during the latter part it is re-evaporated.

The heat exchanges which take place in the steam-engine cylinder produce losses which are of too complicated a nature to be fully dealt with in a short article. The subject can only be touched on very briefly. The losses are, in practice, lessened by surrounding the steam cylinder with steam at the full boiler pressure, or by steam of a higher pressure, thereby keeping the walls of the cylinder at a higher mean temperature than that of the steam passing through the cylinder, and also by expanding the steam in more than one cylinder, or in what is called a compound engine.

The horse-power of a steam engine was fixed by James Watt to be 33,000 lbs. raised 1 foot high per minute.

Let a = the area of the piston in square inches.

Let s = the number of feet per minute the piston travels.

Then the indicated horse-power is

$$\frac{a \times s \times p}{33000}.$$

In practice the actual horse-power given out by steam engines varies from 75 to 95 p.c. of the indicated horse-power, 5 to 25 p.c. being lost by the useless resistance of the engine itself.

One pound of best Welsh coal will evaporate in a good Lancashire or Cornish boiler $10\frac{1}{2}$ lbs. of water, if the feed water is introduced at 100°F.

The consumption of steam or feed water per indicated horse-power per hour by the best expansive working engines may be taken to be approximately as follows:

	Weight of steam or feed water per I. H. P. per hour.
Single cylinder, non-condensing engines	30 to 40 lbs.
Compound cylinder, non-condensing engines . .	20 to 30 „
Single cylinder, condensing engines	18 to 25 „
Compound cylinder, condensing engines	16 to 20 „

To find the quantity of condensing water required for a given engine, it is only necessary to know the quantity of feed water or steam used by the engine and the pressure of steam. A reference to the steam table will enable one to find the total heat-units in the steam used; all that heat must be taken up by the condensing water in raising it from 60°, the normal temperature of the atmosphere, to 100°F., or in raising it 40°. One pound of water then takes up 40 heat-units, and 1 gallon 400 heat-units.

Steam boilers.

Cornish boilers are cylindrical, with a cylindrical flue tube through from end to end; a medium-size boiler is 5 feet in diameter and 24 feet long, with a flue tube 2 ft. 9 in. diameter. The first 6 feet of the flue tube is occupied by the fire grate, having a surface of 16·5 square feet.

Lancashire boilers are similar in construction to Cornish boilers, except that they have two flue tubes instead of only one. Large factory boilers are usually 7 feet diameter by 30 feet long, having two flue tubes, each 2 feet 9 inches diameter. Such a boiler would have a total fire grate surface of 33 square feet, and would burn from 10 to 15 lbs. of coal per square foot of fire grate per hour.

Taking a consumption of 10 lbs. per square foot, the coal burnt per hour would be 330 lbs.

Such a boiler would evaporate 9 lbs. of water from 60°F. per 1 lb. of coal, so that the evaporation of water would be, on the above estimate, 2,970 lbs. per hour.

A fairly economical engine should give an indicated horse-power with 20 lbs. of steam per hour. The indicated horse-power produced from such an engine using the said boiler would be

$$\frac{2970}{20} = 148 \text{ indicated horse-power.}$$

Priming. A boiler is said to prime when particles of water are carried from it to the engine by the steam. Priming may take place because of too rapid an evaporation from a given area of water surface, or because of particles of solid matter, or oil or grease, on the water.

Water for feeding steam boilers should be clean and almost free from solid impurities. Hard water causes incrustation; distilled water, and rain water which has flowed over peaty soil act very injuriously on the rivets and plates of boilers. The action is corrected by the addition of a very small quantity of lime.

Boiler efficiency. A good Cornish or Lancashire boiler will utilise in evaporation 10,500 heat-units with coal which gives off 14,000 heat-units per lb. during combustion, or, in other words, will give an efficiency of 75 p.c.

Steam diagrams.

We get our knowledge of what actually takes place in a steam-engine cylinder from the indicator. This instrument is illustrated by fig. 2. It consists of a drum *a* (on which is fastened a sheet of paper) made to partly rotate backward and forward on its axis by means of a cord connection *b* to a moving part of the engine, having the motion of the piston on a reduced scale. At the side of the drum is placed a small cylinder *c* having a piston held down against the steam pressure by a spring of known tension. Let the piston be one square inch in area, and the tension of the spring 30 lbs. to the inch; then a pencil attached to the piston would indicate by its position the pressure of steam on the piston, at a scale of 30 lbs. per square inch.

The pencil is made to mark a horizontal line on the paper before the steam is turned on to the indicator piston; that line is termed the atmospheric line, as it indicates the pressure of the atmosphere. The indicator being attached to one end of a steam cylinder by means of a pipe, and the drum being made to turn by the engine, the pencil is caused to describe a figure on the paper of the drum like that on fig. 1, in which the horizontal length represents the stroke of the engine on a reduced scale, and the vertical height the pressure of steam in the cylinder at all parts of the engine stroke. It is evident that the area of the figure represents the total force exerted behind the engine piston, and the average height of the diagram the average pressure of steam during that stroke. The average height—or, in other words, the average pressure—is obtained by the ordinary method of measuring irregular figures.

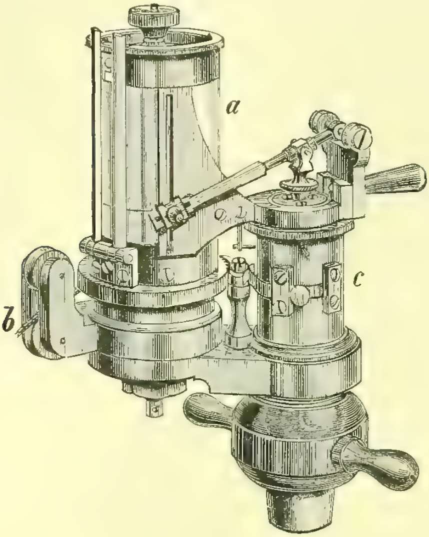


Fig. 2.

This is the practical method of indicating a steam engine. When a great number of diagrams have to be measured, a planimeter is often employed. Having found the average pressure of the steam, the indicated horse-power is obtained by the formula already given.

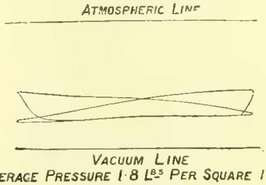


Fig. 3.

The friction of an engine for a given speed can be ascertained from the indicator. It is only necessary to run the engine at that speed without employing it to do any work, and then to take an indicator diagram: the diagram will give the measure of the power absorbed by the engine in overcoming its own friction, and is called a friction diagram. An example is given in fig. 3.

Fig. 4 is a diagram from a Cornish engine. The Cornish engine is single-acting, the work being done on one side of the piston only.

Steam is admitted at *a*, it is cut off at *b*, expanded to *c*, then communication is opened from the active side of the piston to the other side; in other words, the piston is placed in equilibrium for the return stroke till it gets to *d*, then the equilibrium valve is closed, and the steam is compressed in the remaining space, raising its pressure to *a*. The small diagram below is taken from the opposite side of the piston, the top line representing the pressure on the equilibrium stroke, and the bottom line the back pressure of the condenser.

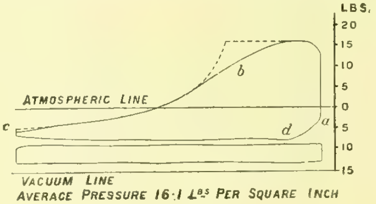


Fig. 4.

In numerous cases of expanding steam in an engine cylinder, there is a deficiency of pressure (from Boyle's law) in the former part of the stroke, and an excess of pressure towards the end of the stroke, as indicated by the dotted line in figs. 4 and 5. The sides of the cylinder being colder than the entering steam, a certain portion is condensed, to be re-evaporated after the cut-off has taken place. It is evident that any water found in the cylinder, or brought over with the steam, will be at the temperature of the steam, and a portion of it, at least, will be re-evaporated on a fall of pressure, partly from its own heat and partly from the heat of the cylinder walls. This re-evaporation is especially the case if the cylinder is surrounded by a steam jacket.

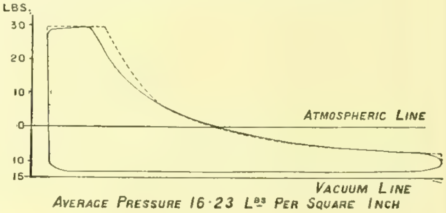
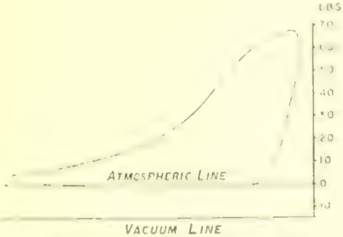


Fig. 5.

During the exhaust stroke of the engine the cylinder is reduced in temperature by the influence of the cold condenser, or, in the case of non-condensing engines, by the exhaust steam. That influence is mitigated in the Cornish engine by its being single-acting, and only exhausting into the condenser from one end of the cylinder—viz. that remote from the end which receives steam from the boiler. This is an element of economy in the Cornish engine.

The diagram (fig. 5) is an example of considerable expansion in a single-cylinder rotative engine.

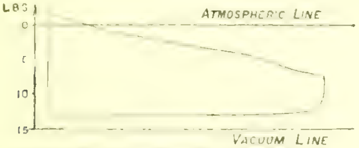
Figs. 6 and 7 are diagrams from the high and low pressure cylinders, respectively, of a modern compound pumping engine. The boiler pressure here employed is 80 lbs. per square inch. The steam is first expanded in one cylinder, and then further expanded in the second.



AVERAGE PRESSURE 27·3 LBS PER SQUARE INCH

FIG. 6.

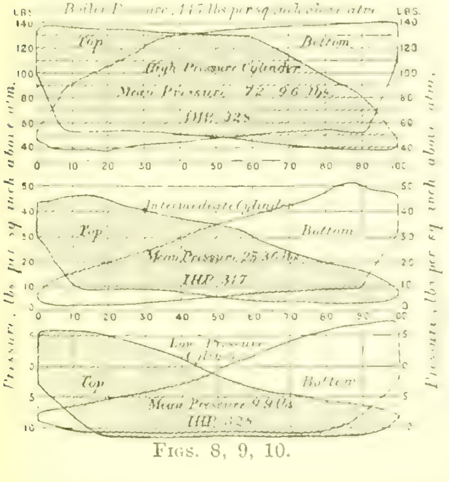
In the Navy it has been found that working with much higher pressures, and greater ranges of expansion, it is more economical to use three cylinders, or what are called triple-expansion engines.



AVERAGE PRESSURE 10·3 LBS PER SQUARE INCH

FIG. 7.

Examples of diagrams from such engines are shown in figs. 8, 9, and 10, which are from the first, second, and third cylinders, respectively of a modern triple-expansion marine engine.



FIGS. 8, 9, 10.

The steam engine, with all engines operated by heat, may be classed under the general term 'heat engines.'

Heat and mechanical energy are mutually convertible. A piece of iron becomes hot by hammering it. The mechanical energy of the blow of the hammer is lost as mechanical energy, but reappears in the iron struck in the form of heat.

Dr. Joule determined the mechanical equivalent of one unit of heat to be 772 lbs. raised 1 foot high.

Steam is simply the agent by means of which heat is made to produce mechanical work. Other substances may be used—such as air in the hot-air engine, and a mixture of gas and air in the gas-engine—but in all cases for every 772 units of work done one unit of heat disappears. All heat engines are very imperfect—that is, they only convert a small portion of the total heat employed into work. In the steam engine, heat is received in the steam from the furnace, and passes through the engine, a portion becoming mechanical energy in the work done by the engine, and the remainder passing away, in the case of a non-condensing engine, into the atmosphere as exhaust steam, and in the case of the condensing engine into the water of the condenser. The heat so passing away is termed 'rejected' heat.

There is a fall of temperature between the inlet and outlet pipes of the engine, or between the heat received and the heat rejected. This fall in temperature produces mechanical work. It may be illustrated by the familiar example of water falling from one elevation to another over a water-wheel, and thereby producing mechanical work. In the case of the steam-engine, it is only possible theoretically to convert a portion of the heat into work, because the lowest temperature at which the steam can be rejected is that of the atmosphere, or normally 60°F. In practice, the temperature must be much higher, 212°F. for non-condensing engines, and about 100° for condensing engines.

In 1824 Sadi Carnot enunciated the great principle that the highest possible efficiency of heat engines, whatever their working substance, is expressed by $\frac{T-t}{T}$, in which T and t are the highest and lowest temperatures between which the engine works, $\frac{T-t}{T}$ expressing the fraction of total heat available for the production of work.

T and t are absolute temperatures, the zero of which is 461° below the zero of Fahrenheit's scale.

Taking steam at 80 lbs. boiler pressure, or 94·7 lbs. absolute, and using it in a condensing engine, in which the exhaust temperature is 120°F., then $\frac{T-t}{T}=\frac{785-581}{785}=\cdot 259$, which represents the heat efficiency of a perfect engine working between the temperatures 324 F. and 120 F.

A superior condensing steam engine, working with say 94·7 lbs. absolute pressure, will use 15 lbs. of feed-water per indicated horse-power per hour—that is, 15 lbs. per 33000 × 60 = 1980000 units of work; dividing by 772, Joule's equivalent, we have 2564 as the equivalent units of heat, or about ·14 of 17700, the heat-units in 15 lbs. of steam at 94·7 lbs. pressure.

According to Carnot's theorem, the fraction of heat available for the production of work in the above example is 17700 × ·259, and the real efficiency of such an engine using 15 lbs. of steam per indicated horse-power per hour is

$$\frac{\text{work done}}{\text{work available}} = \frac{1980000}{17700 \times \cdot 259 \times 772} = \cdot 559.$$

The steam engine is deficient as a heat engine, in that it does not work with a greater range of temperature.

In the steam-engine work is done by a change in the volume of the steam, and theoretically the greatest efficiency is reached when the whole of the change of volume takes place in the engine itself; that is to say, when the steam has been expanded down to the atmospheric pressure in non-condensing, and to the back pressure in condensing engines.

Steam may be regarded as a perfect gas, for the purpose of an approximate generalisation; but as it is generally found in the steam-engine, it is a mixture of steam and water. It is used in a highly-conducting cylinder, giving rise to complicated actions, the results of which have been more satisfactorily determined by experiment than by theory.

Properties of saturated steam.

Total pressure per sq. in.	Temperature in Fahr. degrees	Total heat, in Fahr. degrees from water at 32°F.	Latent heat, Fahr. degrees	Density, or weight of one cubic foot	Volume of one pound of steam	Relative volume, or cubic feet of steam from one cubic foot of water
lbs.	Fahr.	Fahr.	Fahr.	lbs.	Cubic feet	Rel. vol.
1	102·1	1112·5	1042·9	·0030	330·36	20,600
5	162·3	1130·9	1000·3	·0138	72·66	4,530
10	193·3	1140·3	978·4	·0264	37·84	2,360
14·7[1]	212·0	1146·1	965·2	·0380	26·36	1,642
20	228·0	1150·9	952·8	·0507	19·72	1,229
25	240·1	1154·6	945·3	·0625	15·99	996
30	250·4	1157·8	937·9	·0743	13·46	838
35	259·3	1160·5	931·6	·0858	11·65	726
40	267·3	1162·9	926·0	·0974	10·27	640
45	274·4	1165·1	920·9	·1089	9·18	572
50	281·0	1167·1	916·3	·1202	8·31	518
55	287·1	1169·0	912·0	·1314	7·61	474
60	292·7	1170·7	908·0	·1425	7·01	437
65	298·0	1172·3	904·2	·1538	6·49	405
70	302·9	1173·8	900·8	·1648	6·07	378
75	307·5	1175·2	897·5	·1759	5·68	353
80	312·0	1176·5	894·3	·1869	5·35	333
85	316·1	1177·9	891·4	·1980	5·05	314
90	320·2	1179·3	888·5	·2089	4·79	298
95	324·1	1180·3	885·8	·2198	4·55	283
100	327·9	1181·4	883·1	·2307	4·33	270

[1] Atmospheric pressure.

H. D.

STEARIC ACID. *Cetyl acetic acid v.* FATTY ACIDS.

STEARIN and COMMERCIAL STEARIC ACID. The term *stearin* is properly applied to the normal propenyl ether or glyceride of stearic acid, which constitutes the principal solid constituent of most fats. It is, however, used generically to indicate the solid part of any fat from which the liquid portion has been expressed, so that we have *lard* or '*solar*' *stearin*, *olive oil stearin*, *cotton* or *vegetable stearin*, *palm stearin*, and many others. Stearic acid is also almost invariably known commercially as 'stearin.' Glycerin has the power of combining with stearic acid in three proportions, with production of mono-, di, and tri- stearin respectively. The latter constitutes the stearin of natural fats, and is the only one of technical interest.

Mono-stearin $C_3H_5(C_{18}H_{35}O_2)(HO)_2$ is obtained by heating a mixture of equal parts of stearic acid and glycerin at 200° in a sealed tube for about thirty-six hours (Berthelot, A. Ch. [3] 41, 226). The free acid is then neutralised by the addition of lime, and the mono-stearin is dissolved out by ether, from which it separates in white needles melting at 61°.

Di-stearin $C_3H_5(C_{18}H_{35}O_2)_2HO$ is obtained by heating mono-stearin with three parts of stearic acid for three hours at 260°. When separated similarly to mono-stearin, it forms white, microscopic laminæ, melting at 58° and solidifying at 53° (Berthelot, *l.c.*).

Tri-stearin $C_3H_5(C_{18}H_{33}O_2)_3$, hereafter called stearin, can only be obtained in a state of purity by heating mono-stearin for three hours at 270° with 15 to 20 parts of stearic acid in a sealed tube (*v.* Berthelot, *l.c.*; Heintz, A. 92, 300). It may be obtained almost pure by recrystallising the tallow from *Brindonia indica* or *Bassia Parkii* (Bouis and Pimentel, C. R. 44, 1355). Even repeated crystallisation of ordinary stearin fails to free it from palmitin and other glycerides, though its melting-point may be considerably raised (Duffy, C. J. 5, 193 and 303). Stearin crystallises from ether in tasteless, odourless, neutral, white, shining nodules, needles or tables, which volatilise almost unchanged *in vacuo*. It is not perceptibly soluble in alcohol of 30°Bé., nor, in the cold, in alcohol of 97 p.c., but is readily soluble in hot alcohol. The crystals, which separate in flocks, contain alcohol even after prolonged fusion. It dissolves freely in hot ether, and, to the extent of 1 part in 225, in cold ether (Lecanu, A. 12, 25). Volatile oils, carbon bisulphide, and melted camphor also dissolve it. It is readily saponified by alkalis, lead oxide, and other bases.

The abnormal behaviour of stearin under the action of heat has been examined by Kopp (A. 93, 194), Heintz (J. pr. 48, 382), and Duffy (C. J. 5, 193 and 303). When heated from 0° to 55° 1 vol. expands to 1·0308 vols., fusing and contracting to 1·0076 vols. at the latter temperature. On further heating, it expands to 1·1293 vols. at 71·6°, and re-solidifies and again contracts to 1·0759 vols. at that temperature. After re-fusion, it solidifies to an indistinctly crystalline mass at 70°. Duffy (*l.c.*) attributes these changes to the existence of three modifications of stearin having different melting-points, and convertible one into the other by change of temperature, but Bouis (A. Ch. 44, 156) disagrees with this view.

Pure stearin remains unchanged in the air, but the commercial product becomes rancid, probably on account of the presence of olein.

True stearin, which has now become almost superseded by stearic acid for candle-making, &c., is obtained from tallow by removal of the fluid olein by pressure, as described hereafter regarding stearic acid (*v.* also MARGARINE).

The earlier chemists devoted considerable attention to the treatment of animal fats, repeated distillation in steam, and even from dry slaked lime, being commonly practised by them as a method of purifying fats and oils for medicinal purposes. The fact that an oil was obtained by treating soap with an acid was also known, though no difference, except its readier solubility in alcohol (Geoffroy, Phil. Trans. 1742, 42, 71), appears to have been recognised between this oil and the fat from which the soap was originally prepared. The existence of glycerin in the liquid portion of the product of the action of litharge and other basic oxides on fats was shown in 1779 by Scheele (Opuscula Chimica et Physica, i. 125; ii. 175).

The true nature of animal fats was first shown by Chevreul ('Recherches Chimiques sur les Corps Gras,' &c., Paris, 1823), who, in conjunction with Gay-Lussac, took out in 1825 a French patent for the manufacture of stearic acid, Gay-Lussac also taking out a similar patent in England in the name of M. Poole (No. 5,183, 1825). These patents mainly consisted in the saponification of the fat by potash or soda, and the treatment of the resultant soap by hydrochloric or other mineral acid, but also included saponification by lime, and the distillation of the acids by steam. Their process was not commercially successful, but was soon rendered workable by De Milly and Motard (*v.* Payen, Bull. de la Soc. d'Encouragement de l'Industrie, 1833, 156), who saponified the tallow with lime and decomposed the resultant soap with sulphuric acid.

Fats may also be decomposed into glycerin and fatty acids, without the intermediate production of a soap, by the action of steam or water at high temperatures, but the production of acrolein at these temperatures renders the process objectionable. Dubrunfaut, however (*v.* Pat. No. 8,854, 1841, taken out in the name of W. Newton), found it to be workable when the fat is first treated with sulphuric acid and washed. Among other patents based on this process may be mentioned those of G. Gwynne and J. F. Wilson, Nos. 9,944 and 10,000, 1843, and of W. C. Jones and G. F. Wilson, No. 9,542, 1842.

The hydrolysis or saponification by water at high temperatures (approaching the melting-point of lead) was patented by R. A. Tilghman (No. 47, 1854), who heated an emulsion of the fat with one-third to one-half its bulk of water in a series of iron tubes, but this process was not a success, and was soon superseded by De Milly's autoclave process (Pat. No. 2,740, 1856), which is really a combination of Tilghman's and the lime saponification process. Several modifications of the autoclave process are in use.

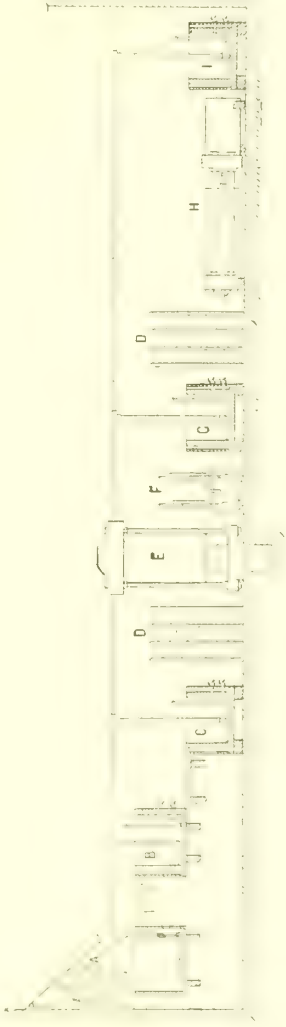


Fig. 1.

The fact that fats were converted into a 'fat' which was soluble in alcohol, by the action of sulphuric acid, was known to Achard in 1777 (*v.* Aikin's Dict. of Chemistry, 1807 [2] 177. The subject was investigated by Caventou, J. Ph. 11, 19), Chevreul ('Recherches Chimiques sur les Corps Gras' &c.), and Fremy (C. R. 2, 467, and 4, 846), and the method of preparing stearic acid, thus elaborated, has been applied commercially by D'Arcet (Q. J. S. 1828, 26, 197), and by Knab (*v.* Bouis, Wurtz, Dict. de Chim. [2] 1651), and De Milly (Pat. No. 1,626, 1866), and, as above, in combination with the treatment with superheated steam and water. It has also been modified by J. C. A. Bock (*v.* Pat. No. 419, 1869; Le Génie Industriel, 40, 311; D. P. J. 208, 230; C. R. 80, 1142; Carpenter, C. C. 1872, 744). Bouis (Wurtz, Dict. de Chim. [2] 1652) criticises Bock's process adversely.

In De Milly's lime saponification process, as now carried on, the tallow is melted with about 15 p.c. of water in a lead-lined tun B (fig. 1), or in a cemented brick reservoir, and is heated by steam passed in through a perforated spiral tube, and mixed by teeth on arms carried by a continuously-revolving shaft in the tun. A thin cream of lime free from iron is then added from a tub A, so that the fat is gradually saponified, the calcium stearate and oleate separating after three or four hours as an insoluble greyish soap known as 'rock.' The mixture is allowed to settle when the rock crumbles in the fingers without feeling fatty, *i.e.* after five or six hours. The amount of lime used formerly amounted to 16 p.c. of the fat, but has now been considerably reduced.

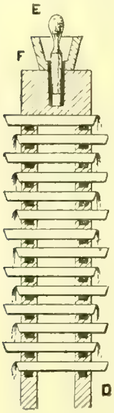


FIG. 2.

The rock is dug out, and is heated and agitated in a similar tun C, with about 24 parts of sulphuric acid of sp.gr. 1·85, diluted to 1·17 or 1·20 sp.gr. for every 100 parts of tallow treated, and the mixture is allowed to settle. The dingy, brownish layer of fatty acids is next skimmed off, and washed with water heated by a steam jet, sometimes with previous agitation with sulphuric acid of 4° to 5°Bé., and is then run into a trough F (fig. 2), whence it passes through funnels, each capable of being closed by a plug E, into the uppermost of a series of trays arranged in a framing D (fig. 1), so that the spout of each projects over the tray beneath. Thus the liquid runs from tray to tray until all are filled. The trays are kept in a room at 20–30°C. for two or three days until the acids become granular, and the cakes produced are placed in woollen or horsehair cloths and cold-pressed in a press E, the pressure being largely increased when the oleic acid ceases to flow easily. The nearly white stearic acid thus obtained is melted by steam, settled, drawn off and cooled in dishes at about 30°C. until crystalline, and is then rasped up into a meal and again pressed in hair or woollen bags in a hot press H, having hollow plates heated by steam or hot water, and kept at 95–104°F. A pressure of 12,000 lbs. and a temperature of 120°F. is sometimes used for pressing the products from the best tallows.

The cakes thus obtained are hard and white, and contain oleic acid round the edges, and are therefore scraped all over, melted in a vat I, and cast into blocks.

The total yield of fatty acids varies between 92 and 95 p.c. of the tallow, and the stearic acid averages about 46 p.c. of the fatty acids.

As the gypsum obtained in the working is worthless, it has been proposed to replace the lime by baryta, which produces barium sulphate in a condition suitable for use as a pigment, or by alumina in the form of sodium aluminate, which yields aluminium sulphate as a by-product.

Fig. 3 shows an arrangement for removing most of the stearic acid which remains in the oleic acid expressed as above. The acid is placed in a trough *f*, into which dips a revolving drum A, through which circulates cold water. The acid is thus carried round in a thin layer, and solidifies on the surface, from which it is removed into a reservoir F by a scraper *h*. The mass is pumped thence through a filter press, so that a further yield of about 4 p.c. of stearic acid is obtained, together with clearer and more valuable oleic acid (D. P. J. 263, 48).

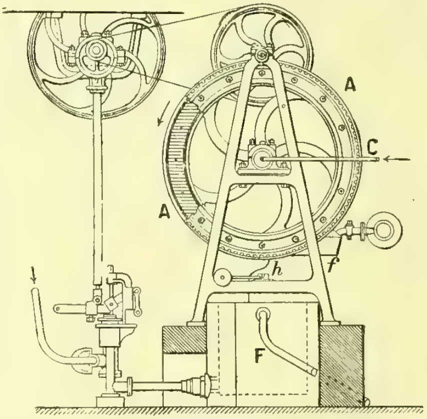


FIG. 3.

The large amount of sulphuric acid required in this process, together with the discoloured nature of the product, has caused De Milly's autoclave process to be largely employed. This consists in treating the fat, at a pressure of about 8 atmospheres, in an autoclave (*v.* AUTOCLAVE, i. 223), so that the action is assisted by that of the water. The proportion of lime used may thus be reduced to about 2 p.c., while its presence permits of saponification at workable pressures instead of the high pressures necessary when water or steam is used alone.

The steam enters the autoclave at about 8 atmospheres pressure, through a tube passing to the bottom of the autoclave, and is supplied continuously for five or six hours when, after standing for two hours, the glycerin is withdrawn, followed by the fatty acids mixed with lime soap. The mixture is treated with 60 lbs. of sulphuric acid of 66°Bé. diluted to 14° or

15°Bé., for every 1,000 lbs. of tallow treated, steam being supplied for two hours, after which the acids are settled and washed.

According to Buff (Bl. ii. 1864, 308), the presence of a little caustic soda facilitates saponification in the autoclave.

In the process of Michaud Frères the lime is replaced by zinc oxide amounting to from 0·2 to 0·6 p.c. of the fat, and supplied in the form of zinc white, or of the mixture of zinc-dust and oxide obtained in the zinc manufacture. A product of superior whiteness results from this process (Poullain and Michaud's French Pat. No. 151,404, 1882).

In a modification of this process, a rod of metallic zinc is fitted in the autoclave, and 1 p.c. of lime is mixed with the fat (J. H. Clinton, U.S. Pat. No. 336,795, 1886).

Several modifications of the autoclave process are in use where the decomposition is effected by steam or water, as in Tilghman's process, without the aid of lime or other agents, the pressure, however, requiring then to be about doubled.

Fig. 4 shows the arrangement employed by A. Michaud (Pat No. 8,403, 1885; *v.* also Lach., Chem. Zeit. 13, 1218). A mixture of 5 parts of tallow to 1 of water is supplied by a montejus A, through pipes, to autoclaves B B′, having pipes $x\,x'$ $y\,y'$, which open into a vessel C, so that when the mixture is heated, the pressure, which rises to about 15 or 16 atmospheres, forces it through the pipes $y\,y'$ into that vessel, whence it passes back through the pipes $x\,x'$, and is thus continuously circulated.

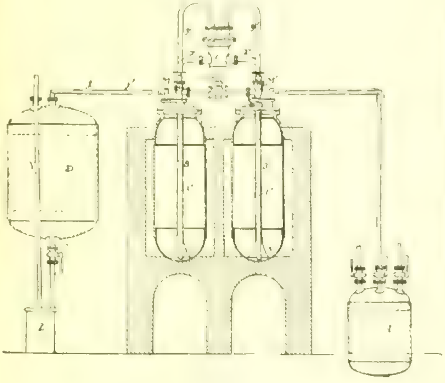


Fig. 4.

After about eight hours, the mixture of fatty acids and glycerin is discharged into a closed vessel D, from which, after settling for half-an-hour, the glycerin is drawn off at *o*.

D'Arcet's process of saponification, introduced in 1828, consisted in heating the fat at a temperature of 105–110°C. in a closed vessel with about 1 p.c. of sulphuric acid diluted with 20 to 50 parts of water. This was followed by a process patented by L. H. F. Melsens (No. 2,666, 1854), for saponifying with water acidulated with 1 to 10 p.c. of sulphuric acid at 180–200°C. in an autoclave.

The saponification by sulphuric acid at ordinary pressures is particularly applicable to rancid or partly-decomposed fats, such as bone fat and slaughter-house, kitchen, and other refuse.

The fat is mixed with from 6 to 15 p.c. of concentrated sulphuric acid, and is heated in a lead-lined vessel by a steam coil to 212° or even 320°F. for fifteen or twenty hours. Offal fat usually requires 12 p.c. of acid, and palm oil 6 per cent., for its decomposition. The mass swells up and becomes black, with evolution of much sulphurous acid, as much as 16 to 20 p.c. of the fat being destroyed in the case of the cruder kinds.

The black product is freed from sulphuric acid by washing, and the fatty acids are purified by distillation.

Knab's process, introduced in 1855, consisted in reducing the time of action of the acid to about two minutes. The fat and about half its weight of sulphuric acid of 66°B. were separately heated to 90°C. and rapidly mixed, and after two minutes thrown into water. The process was unworkable on account of the large quantity of sulphuric acid used.

A very similar process was introduced in 1867 by De Milly, who allowed the fat, heated to 120°C., to mix in a thin stream with 6 p.c. of strong sulphuric acid, with brisk stirring, the mixture being run into boiling water after about two or three minutes. The dark colouring matter produced is soluble in oleic acid, so that the subsequent cold and hot pressing gives cakes of nearly white 'stearin.'

Bock's modification of the sulphuric acid process, which is largely used on the Continent, consists principally in the means employed for removing the dark colouring matters from the fatty acids, the whole operation being conducted at a comparatively low temperature. In the original process the fat is treated with strong sulphuric acid to remove the membranous envelopes of the fat cells, and the product is heated at 100°C. with 4 to $4\frac{1}{2}$ p.c. of sulphuric acid diluted with water to complete the saponification. The resultant product is then continually agitated and heated by a steam coil for several hours, after addition of oxidising agents, such as bleaching powder or potassium bichromate or permanganate, to oxidise and render the colouring matter denser.

After twelve or sixteen hours settling, the liquid is decanted from the black deposit, and is re-heated for two or three hours with acidulated water, boiling being repeated several times with intervals of rest. The resultant fatty acids are said to be as pale as those obtained by lime saponification.

According to Bouis (Wurtz, Dict. de Chim. [2] 1652), the sinking of the colouring matter is due, not to oxidation, but to its segregation from the agitation of the mass.

A complete process for saponifying the fat, now largely carried on in England, is as follows. The fat is pumped from a tank A (fig. 5) into a series of lead-lined tanks B, from which, after heating by steam coils, it is passed into a copper acidifier D, supplied through a valved pipe with steam heated to about 176°C. by a superheater F, and having a water shower-pipe at *d*, for condensing the evolved vapours. After heating for some time, a quantity of sulphuric acid varying from 3 to 6 lbs. per cwt. of tallow, according to the quality of the same, is introduced from a tank E, and the material is left, after saponification is complete, for six hours, and is then discharged into washing vats G, containing acidulated water heated by steam coils and free steam. After two hours' heating, it is settled for twenty-four hours, and drawn off into the tank A, from which it is pumped into a tank H, where it is kept liquid by a steam coil.

About 5 tons of the material is now run into a still I, in which it is heated to about 116°C., and distilled with the aid of superheated steam at about 294°C. The vapours pass to a refrigerator, consisting of a series of copper tubes connected by gun-metal bends and mounted in iron frames over a set of circular iron tanks *k*, into which they can be emptied, and which are fitted with pipes for supplying steam, and with coils for cooling. A shower-pipe L condenses most of the remaining vapours in a tank *l*, and the uncondensed gases pass away by a pipe M, and are burned in the flue. 100 parts of the tallow give about 60 parts of stearic acid ready for use for candle-making without pressure, and about 20 parts which require to be pressed and re-distilled, and which give about three-fourths of stearic acid and one-fourth of oleic acid.

A quantity of pitch which remains in the still is run off into an iron vessel and distilled, thus giving a further quantity of inferior stearic acid. The remaining pitch is said to be used as a substitute for 'Japan black' in coating iron.

A paper by Wilson on the manufactures of Price's Candle Company will be found in the J. Soc. Arts, 4, 148, and a series of papers by Lach on the French Stearin Industry, in the Chem. Zeit. 13, 1157, 1218, and 1335. Field's 'Cantor Lectures on Solid and Liquid Illuminating Agents' (1883), from which figs. 1 and 5 are taken, may also be consulted.

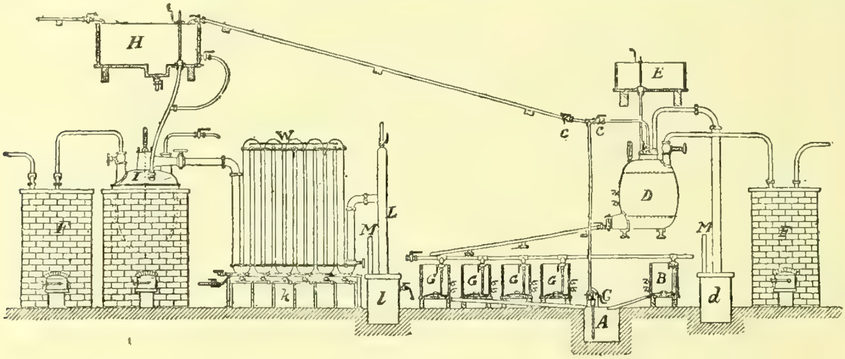


FIG. 5.

In addition to the stearin and stearic acid obtained from tallow, may be mentioned the stearic acid prepared from Yorkshire grease, which is obtained from the soapy waste from the oiling, cleansing, and milling of fibres, yarns and cloths (*v.* Hurst, S. C. I. 1889, 92); *cotton-seed* or *cotton stearin*, obtained by cooling cotton-seed oil to a few degrees above 0°C., is stated by Muter (An. 1882, 98) and others to be used for adulterating lard and tallow and in making margarine; '*solar*' or *lard stearin*, obtained by pressing lard, is used in candle-making (*v.* Wiley, Bull. of the U.S. Department of Agriculture, 13, part 4); *olive oil stearin*, *palm stearin*, and *coco-stearin*, are respectively obtained by cooling and pressing olive, palm, and cocoanut oil.

Processes for bleaching tallow and stearin are described in the article on TALLOW.

G. T. H.

STEAROLAURETIN and **STEAROLAURIN** *v.* LAURUS NOBILIS.

STEATITE. (*Speckstein*, Ger.) A massive or schistose variety of talc, more or less impure, known popularly, from its unctuous feel, as *soap-stone.* It is so soft as to be readily scratched by the finger-nail, its hardness being only 1·5. Hence it is easily carved or turned in the lathe; and this property, coupled with its power of resisting high temperatures, has led to its extensive employment in the arts. In consequence of its use for culinary vessels, it is sometimes known as *pot-stone* or *lapis ollaris.* In India it is wrought into bowls and plates, which, though more expensive than similar articles in earthenware, are purchased by reason of their refractory character. It is also used in parts of India, as at Agra, for ornamental earvings; while the Chinese largely employ it, and similar stones, for a like purpose. Some of the so-called Chinese soap-stone is agalmatolite, or pagodite, while certain other kinds appear to be compact pyrophyllite (A. H. Church, Geol. Mag. 3, 1866, 164; G. J. Brush, Am. S. 2, 26, 1858, 68). In South Africa soap-stone is carved by the natives into tobacco-pipes and nozzles for bellows used in iron-smelting.

Steatite has come into extensive use for gas-burners, for stove-backs, for lining furnaces, and as an ingredient in asbestos goods; while it has also found application as an insulator of electricity. In the East it has long been employed, in a powdered state, as a protective material for coating obelisks, &c. In association with a quick-drying varnish it is said to form a valuable anti-corrosive paint, and has been recommended by F. C. Goodall for naval purposes. Applied to steel ships or bridges, it secures permanent adhesion to the metal and prevents rust.

Steatite is sometimes used in the manufacture of porcelain, and the veins of the mineral in the serpentine of the Lizard, in Cornwall, were formerly quarried for supplying the china works of Bristol. Steatite, like serpentine, has likewise been employed as a source of magnesium salts, especially the sulphate. For its use as a lubricating agent *v.* French chalk; also Talc. (For *Indian steatite v.* Ball, Man. Geol. India, 3, 1881, 439; for *American steatite v.* Merrill, in Smithson. Rep. 2, 1889, 357.)

F. W. R.

STEEL *v.* Iron.

STEPHANITE. *Silver sulphantimonite v.* Antimony.

STIBICONITE. A variety of *Antimony tetroxide* Sb_2O_4 *v.* Antimony.

STIBNITE. *Antimony sulphide v.* Antimony.

STICK LAC *v. Lac resin*, art. Resins.

STILBENE *Toluylene* $C_6H_5.CH:CH.C_6H_5$.

Preparation.—Stilbene has been prepared by a variety of methods, such as the distillation of benzaldehyde with sodium (Williams, C. N. 15, 244) and digestion of benzylidene chloride with sodium (Limpricht, A. 139, 318), or with zinc-dust and alcohol (Lippmann and Hawliczek, J. 1877, 405). Better yields are got by passing the vapour of dibenzyl over heated lead oxide (Behr and Van Dorp, B. 6, 754), by allowing toluene to fall at the rate of 6 drops a minute on to lead oxide, heated to dark redness in an iron tube (Lorenz, B. 7, 1096; 8, 1455; Vincent, C. R. 110, 907), by distilling benzyl sulphide at not too high a temperature (Limpricht and Schwanert, A. 145, 332; Forst, A. 178, 373), and especially by heating the polymeric thiobenzaldehydes at 150–200° (Baumann and Klett, B. 24, 3308), or β-trithiobenzaldehyde (m.p. 225°) with 8–12 times its weight of finely divided copper (Klinger, B. 10, 1878).

Properties.—Stilbene crystallises from alcohol in large, monoclinic tables (vom Rath, B. 5, 624), melts at 121–122° (Forst and Zincke, A. 182, 261), at 124° (Michaelis and Lange, B. 8, 1314), boils at 306–307° with thermometer in vapour (Graebe, A. 167, 158), is volatile with steam, and dissolves readily in ether, benzene, and hot alcohol. When warmed in alcoholic solution with ferric chloride it gives a red colouration (Kade, J. pr. [2] 19, 467). It combines directly with bromine, forming *stilbene dibromide* (m.p. 237°), which on treatment with alcoholic potash is converted into *tolane.* On digestion with fuming sulphuric acid it yields a *disulphonic acid*, which, like its salts, dissolves readily in water (Limpricht and Schwanert, *l.c.*). When its vapour is led through a red-hot tube a mixture of *toluene* and *phenanthrene* is obtained (Graebe, B. 6, 126).

Stilbene, like ethylene, of which it may be regarded as the diphenyl- derivative, yields a number of stereo-isomerides (*cf.* Reimer, B. 13, 742; Rügheimer, B. 15, 1626; Wislicenus, Abhandlungen der K. Sächs. Gesell. der Wissensch., math.-phys. Klasse, 14, 22; Blanck, A. 248, 1; Bischoff, B. 21, 2071), which, however, cannot be described here.

Orthodinitrostilbene, prepared from orthonitrobenzyl chloride by the method employed in the case of the para- derivative, exists, according to Bischoff (B. 21, 2071), in two isomeric forms, melting at 126° and 196° respectively, the latter being the chief product.

Paradinitrostilbene is obtained by heating a warm alcoholic solution of paranitrobenzyl chloride with excess of aqueous caustic potash and crystallising the flocculent precipitate from nitrobenzene (Strakosch, B. 6, 328). It crystallises in yellow needles, sublimes in yellow scales, does not melt at 280°, and is tolerably soluble in nitrobenzene and hot acetic acid, sparingly soluble in alcohol, and almost insoluble in benzene and ether.

Orthodiamidostilbene is prepared by the reduction of orthodinitrostilbene (m.p. 196°) with tin and hydrochloric acid (Bischoff, B. 21, 2078). The yield of pure base amounts to about 50 p.c. of the theoretical. It crystallises from alcohol in large, thin, golden prisms, and from ether in short, thick prisms, melts at 176°, and in alcoholic or ethereal solution exhibits a marked violet-blue fluorescence. Its disazo- colouring matters do not differ much in shade from the corresponding dyes from paradiamidostilbene, but are not as fast to soap (Bischoff, *l.c.*).

Paradiamidostilbene is obtained from paradinitrostilbene by reduction with alcoholic ammonium sulphide (Strakosch, *l.c.*), or with stannous chloride or tin and hydrochloric acid (Klinger, B. 16, 943; Actieng. für Anilinfab., Germ. Pat. 39756 of May 22, 1886; Bender and Schultz, B. 19, 3237; Elbs and Hörmann, J. pr. [2] 39, 502). It crystallises from alcohol in lustrous yellow needles or scales, sublimes in scales, melts at 227°, and dissolves sparingly in hot water and benzene, but easily in alcohol. Ferric chloride colours the alcoholic solution bluish-green. The *hydrochloride* and *sulphate* are crystalline and somewhat sparingly soluble in water. The *diacetyl-* derivative crystallises from alcohol in nacreous scales, and melts at 312° (Bender and Schultz, *l.c.*). By interaction with the naphthylamine- or naphthol-sulphonic acids tetrazostilbene gives disazo-colouring matters which respectively give shades of red or blue on cotton (Actieng. für Anilinfab., *l.c.*; Germ. Pats. 43142 of March 22, 1887; 43197 of April 20, 1887; 46971 of March 29, 1888; 47026 of Sept. 14, 1888).

Paradiamidostilbenedisulphonic acid is obtained by the reduction of the product formed by the condensation of paranitrotoluenesulphonic acid in the presence of alkali. 50 kilos. of sodium paranitrotoluenesulphonate are dissolved in about 700 litres of water, and digested with about 30 kilos. of aqueous caustic soda of 40 Bé. The colour changes from saffranine-red to an intense yellow-red, and the condensation compound, probably azoxystilbenedisulphonic acid[1] (*cf.* Witt, B. 25, 80), can be salted out from the solution. The reduction is effected by boiling the alkaline liquid with zinc-dust until decolourised, filtering hot, and precipitating the amido- acid with hydrochloric acid (Bender and Schultz, B. 19, 3235; Leonhardt & Co., Germ. Pats. 38735 of Jan. 29, 1886; 40575 of Dec. 14, 1886). It is a yellowish, microcrystalline powder, insoluble in water. The *barium* salt is very soluble in water, and is obtained in lustrous, nacreous scales on addition of salt to its aqueous solution. The *tetrazo-* derivative is sparingly soluble in water, and yields a *hydrazine* which, on oxidation with copper sulphate, is converted into a *stilbenedisulphonic acid.* The disazo- dyes formed by the interaction of tetrazostilbenedisulphonic acid with phenol, phenetoïl, salicylic acid, and the naphthylaminesulphonic acids have already been described (*v.* AZO- COLOURING MATTERS; *cf.* also Farbenfab. vorm. F. Bayer & Co. Germ. Pats. 49139 of Dec. 6, 1888; 49950 of Sept. 2, 1888).

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[1] [illegible] Jan. 13, 1888; 48528 of Dec. 20, 1888; Eng. Pat. 2664 of 1888, [illegible]

Dihydrazinestilbenedisulphonic acid is prepared by reducing tetrazostilbenedisulphonic acid with the calculated quantity of stannous chloride in hydrochloric acid solution. It is almost insoluble in water, and on treatment with aromatic aldehydes or ketones in the presence of sodium acetate yields direct cotton dyes, which for the most part produce yellow shades (Actieng. für Anilinfab., Germ. Pat. 46321 of March 18, 1888).

STONE, ARTIFICIAL, *v.* CEMENTS.

STORAX *v.* BALSAMS.

STRAMONIUM *v.* DATURA.

STRASS *v.* GEMS, ARTIFICIAL.

STRASSBURG TURPENTINE *v.* OLEO-RESINS.

STROMEYERITE. *Argento-cuprous sulphide* or *Argentiferous copper glance* AgCuS or $Ag_2S.Cu_2S$. A mineral crystallising in trimetric forms isomorphous with copper glance. Sectile, dark steel-grey colour, shining streak; subconchoidal fracture. H. 2·5–3·0°; sp.gr. 6·2–6·3. *V.* SILVER.

STRONTIANITE. *Native strontium carbonate v.* STRONTIUM.

STRONTIUM. Symbol, Sr. At. w. 87·2.

Strontium derives its name from Strontian, in Argyllshire, where strontianite, the carbonate of strontium, was first found. This mineral was suspected by Crawford in 1790 to contain a new earth, the existence of which was confirmed by Hope in 1792, and by Klaproth in 1793. The metal strontium was first isolated by Sir Humphry Davy in 1808.

All primary rocks contain strontium in greater or less quantity. More strontium than barium has been taken up by water, owing to readier solubility of the sulphate, which is found deposited along with gypsum on evaporation. The carbonate and sulphate of strontium are often found along with deposits of common salt (Dieulafait, A. Ch. [5] 15, 530).

Strontium is chiefly found as the sulphate, *celestine* $SrSO_4$, and the carbonate, *strontianite* $SrCO_3$. It almost invariably accompanies calcium in traces in the various forms of aragonite and calcite. In *barytocelestine* it occurs along with barium as a mixed sulphate; barytes also generally contains traces of strontium. *Brewsterite* $Al_2O_3.H_4(BaSr)O_3.(SiO_2)_6 + 3H_2O$ is a silicate in which strontium occurs associated with barium. Strontium, in minute traces, is present in the mineral waters of Carlsbad, Kaiser-Franzenbrunnen, and many other places, and in seawater.

Metallic strontium was obtained by Davy by the electrolysis of the moistened chloride or hydroxide. The pure metal is best obtained by electrolysis of the fused chloride according to the method employed by Matthiesen and Bunsen. The anhydrous chloride of strontium, mixed with a little ammonium chloride, is placed in a porcelain crucible, having a porous cell in the middle, in which is placed the negative pole, consisting of a thin iron wire wound round a thicker one and covered by a piece of tobacco-pipe stem, so that only one-sixteenth of an inch of it appears below. The level of the salt in the porous cell is considerably higher than that in the crucible. The positive pole consists of an iron cylinder surrounding the porous cell, within the crucible. The chloride is then gently fused, the temperature being regulated so that a crust forms upon it, under which, when the electric current is passed, the metal collects in pieces sometimes half a gram in weight, being protected from the oxidising influence of the air by the crust.

The metal may also be obtained, according to Franz (J. pr. 107, 253), by heating for some time to 90° a saturated solution of the chloride with an amalgam of a kilogram of mercury and 250 grms. of sodium. An amalgam of strontium is thus obtained, which is rapidly washed and dried between filter paper; the mercury is then volatilised by heating in an iron crucible in a current of hydrogen, a regulus of strontium remaining. Caron (C. R. 48, 40) obtains it by fusing the chloride with an alloy of sodium and lead.

Strontium is a yellow metal of a shade somewhat darker than that of calcium. It is also harder than calcium, and oxidises in the air much more readily than that metal. Its sp.gr. is 2·5418. It is malleable, and melts at a moderate red heat; it is more electro-negative than calcium and the alkali metals. When heated it burns brilliantly, forming the oxide, and decomposes water with considerable violence. It also combines with chlorine, bromine, iodine, and sulphur, with evolution of light and heat. Dilute acids readily dissolve it, with formation of the corresponding salts.

Strontium monoxide, or *strontia*, SrO, is obtained when the nitrate is heated to redness, or when the carbonate is ignited, either alone or in contact with carbonaceous matter, such as coal or charcoal. Leplay (D. P. J. 256, 169) having observed that in the decomposition of strontium carbonate by means of superheated steam the hydrate formed loses water at temperatures near its melting-point, and is converted into a solid mass of oxide, has devised a process for production of strontium oxide upon the large scale. Moist strontium carbonate, moulded into suitable forms, is deprived of a portion of its moisture and heated in retorts placed over a decomposing furnace. Superheated steam is also blown into the retorts, and the liberated carbonic anhydride led away. The oxide formed by ignition of the hydrate is removed in waggons, fresh carbonate being introduced in order to make the process continuous.

Strontium oxide is a greyish-white porous mass of sp.gr. 3·9, non-volatile, infusible and glowing with a dazzling white light in the oxyhydrogen flame. It possesses an alkaline taste and reaction. Like lime, when moistened with water it slakes, becoming hot and falling to powder. If the calculated quantity of water be added to form the crystalline hydrate, the whole solidifies to a solid mass.

Strontium hydrate, $Sr(OH)_2$, is the product of the action of water upon the oxide. On dissolving the hydrate in 5–6 parts of boiling water, filtering hot and allowing to cool in a closed vessel, small transparent quadratic crystals of $Sr(HO)_2 + 8H_2O$ are deposited; these deliquesce in the air and are rapidly converted into carbonate. Heated to 100°, 50 p.c. of water is expelled, leaving the hydrate $Sr(HO)_2$. This hydrate may also be obtained in the fused state by heating the crystals to low redness, solidifying on cooling to a greyish-white crystalline mass. At a red heat all the water is expelled, anhydrous strontia remaining. The crystals of

$$Sr(OH)_2 + 8H_2O$$

are soluble in 50 parts of cold and 2·4 parts of boiling water, forming strontia-water, which rapidly absorbs carbon dioxide from the atmosphere, becoming coated with a crust of carbonate.

According to Heyer (B. 19, 2684), when strontium hydroxide is heated to bright redness and the oxide so formed exposed to air saturated with aqueous vapour and afterwards to dry air, a crystalline powder of the composition $Sr(HO)_2 + H_2O$ is obtained. Another hydrate of strontium, $Sr(HO)_2 + 2H_2O$, also exists according to Müller-Erzbach (B. 20, 1628).

Hydrate of strontium is largely used in the preparation and refining of beet-root sugar, and in the extraction of crystallisable sugar from molasses. Its use depends upon the property of the oxide and hydrate of strontium to combine with sugar to form saccharates easily decomposable by carbon dioxide. Lime was formerly used, but strontia is preferable, the precipitated saccharate of strontia being more granular than that of lime. Scheibler (B. C. 1881, 849) shows that to obtain a good yield three molecules of $Sr(OH)_2$ should be employed; if four molecules are used 98·4 p.c. of the sugar is precipitated. For one kilogram of molasses half a kilogram of $Sr(OH)_2$ in one-and-a-half kilograms boiling water is a good proportion. The mixture is stirred, then, after standing nearly a day, the saccharate crystallises out; it is afterwards pressed and washed with cold strontium hydrate. Under increased pressure and temperature a tribasic saccharate is obtained, but if this while hot is introduced into hot water it is decomposed, $Sr(OH)_2$ crystallising out, and the ordinary saccharate $C_{12}H_{22}O_{11}.SrO + 5H_2O$ remaining in solution. On the large scale this clear solution is heated to over 100° when the saccharate is precipitated, impurities remaining in solution. The saccharate is afterwards decomposed by carbon dioxide.

Many processes have been devised for the manufacture of strontium hydroxide, of which the following are the most important:—

In Niewerth's process (D. P. J. 251, 191), celestine ($SrSO_4$) is mixed with equal quantities of coal and brown iron ore and roasted. On lixiviation of the product with water, strontium hydrate and ferrous sulphide are produced.

Claus (D. P. J. 253, 82) proposes to obtain it from the chloride by addition of an equivalent of barium hydrate to the hot solution; $Sr(OH)_2$ crystallises out and barium chloride is recovered by evaporation and crystallisation. Also by adding an equivalent of barium hydrate to a hot solution of strontium sulphide. It is also found that if a solution of barium sulphide is added to a hot solution of strontium sulphide, hydrate of strontium crystallises out on cooling, barium hydrosulphide remaining in solution. A similar reaction occurs between sodium and strontium sulphides. On evaporating the solutions of barium or sodium sulphydrate, mixing with coal-dust, igniting gently and lixiviating, solutions of barium and sodium sulphides are obtained which can be used again. Mother-liquors containing strontium hydrosulphide when evaporated and ignited with coal-dust give strontium hydroxide on lixiviation with water. Claus also (J. Ph. [5] 11, 434) describes a process based on the decomposition of strontium monosulphide into hydroxide and hydrosulphide under influence water, the hydroxide crystallising out.

Leplay's process (D. P. J. 254, 436) consists in treating strontianite ($SrCO_3$) with steam superheated to a temperature higher than the melting-point of the hydrate. The carbonate is introduced into iron pots and there heated to low redness; the contents are then removed tc retorts, into which the superheated steam is blown. The semi-fluid hydrate flows into a suitable receiver, and is thence run off into moulds. It is best to prepare the carbonate by working it into a paste with 30–40 p.c. weak caustic lye, and converting into balls or hollow cylinders.

Knight (Pat. 16,220, 1884) precipitates strontium sulphide with an equivalent of zinc chloride; after decantation from the precipitated sulphide of zinc, the clear solution is decomposed with caustic soda, strontium hydroxide crystallising out on cooling.

Lee Pattinson (Pat. 16,989, 1884) employs the following process: An equivalent of manganese dioxide is added to a solution of strontium sulphide and air of the temperature of 100°F. blown through. About 66 p.c. is converted into hydrate and 33 p.c. into insoluble thiosulphate, 33 p.c. of the sulphur present being also deposited. The sulphur is extracted by naphtha, and the oxide of manganese used again. If air is only blown through until a precipitate begins to form, two-thirds of the Sr is found to be converted into hydrate, and on crystallising almost pure hydrate is obtained. The mother-liquor containing tersulphide is converted to sulphide and used again.

Mactear (Pat. 5,170, 1886) mixes strontium sulphate with slightly more than its equivalent of sodium sulphate and a quantity of carbonaceous matter. The finely-divided mixture is heated in a furnace until the sulphates become reduced to sulphides. The product is treated with hot water, when the two sulphides react, with production of sodium hydrosulphide and strontium hydrate, which latter is obtained by crystallisation. The mother-liquor containing the former is evaporated, and the residue used again in reducing a fresh supply of celestine. The hydrosulphide of strontium obtained as a by-product in the working of the Claus process may be utilised by mixing it with a solution of sodium sulphide Na_2S, when strontium hydrate and sodium hydrosulphide are formed, the former of which may be crystallised out as usual.

According to Trachsel (S. C. I. 1886, 630), other processes for the manufacture of the hydrate from strontianite and celestine are as follows. If the native carbonate is employed as the raw material, it is first converted to oxide in kilns, the burning requiring a higher temperature than that of lime; the resulting oxide is then dissolved in boiling water, the solution clarified and crystallised. If the sulphate is used, the process is more complicated. The powdered mineral may be boiled with a solution of sodium carbonate, and the resulting carbonate made into bricks with sawdust and calcined as above. Or a mixture of strontium sulphate and sodium carbonate may be furnaced, yielding also strontium carbonate and sodium sulphate. In a third process ammonium carbonate is used to convert the sulphate into carbonate, the conversion being accomplished in closed vessels provided with stirring apparatus.

Trachsel, in order to simplify the manufacture, has devised the following more direct process. It is based upon the fact that a solution of strontium sulphide treated with caustic soda becomes converted into strontium hydrate, sodium sulphide or sulphydrate being simultaneously formed

$$SrS + 2NaOH = Sr(OH)_2 + Na_2S$$

or $$SrS + NaOH + H_2O = Sr(OH)_2 + NaHS.$$

The second reaction is most advantageous, requiring only half the soda. The sulphide and sulphydrate of soda are then converted to carbonate by a stream of carbon dioxide:

$$2NaHS + CO_2 + H_2O = Na_2CO_3 + 2H_2S.$$

The sulphuretted hydrogen may be utilised by converting it into sulphur dioxide by passing it through a Claus kiln.

The sodium carbonate is next treated with caustic lime, obtaining thereby calcium carbonate and caustic soda, which can be used again, thus rendering the process continuous.

The sulphate fresh from the mine is passed through a crushing apparatus, mixed with 7 cwts. of coal to every 20 cwts. of sulphate, and the mixture calcined in a plus-pressure or revolving furnace, 3 to 4 hours being sufficient for the conversion to sulphide. It is then carried to the lixiviators, consisting of round or square vats of boiler-plate, each provided at six inches from the bottom with a removable grating of iron bars, on which is spread a filter of sugar bags covered with fragments of brick or other suitable material to protect it from the red-hot furnace charge. In the centre of the grating an upright cast-iron pipe is fixed, passing through the grating but not quite touching the bottom of the vat, and bearing on the top a flat or umbrella-shaped plate, between which and the pipe an interstice is left for the escape of liquor which is forced up by the steam entering through a steam-pipe placed in the centre of the cast-iron pipe at the bottom of the vat, over which it projects several inches. In these vats the charges as they come from the furnace are covered with boiling water or weak liquor from a former operation, and the steam is turned on, which not only keeps the liquor boiling, but also circulates it energetically, forcing the liquor which has percolated through the false bottom upwards in the cast-iron pipe, when it falls back upon the charge. When the liquor has attained the strength of 24°Tw. it is allowed to settle, and then run off to crystallising tanks, where it is treated with a strong solution of caustic soda. The greater part of the hydrate of strontium falls down at once, a further quantity crystallising out on cooling. The mother-liquor (chiefly NaSH) is drained away from the crystals and run into evaporating pans, where it is concentrated to 30°Tw. and again run into other crystallising tanks, where it deposits practically all its strontium hydrate.

The crystals are dried and washed in hydro-extractors and twice re-crystallised, which renders them ready for packing. This double re-crystallisation causes serious loss, but by the following device one re-crystallisation is found sufficient. The impure hydrate, after being once dried and washed is thrown into a muffle-furnace, where it is gently heated and stirred about. Part of the water of crystallisation is thus driven off, the sulphide of iron is oxidised, and any sulphide of strontium is changed to sulphite, sulphate, and thiosulphate, a little carbonate of strontium being also formed. This carbonate is sufficient to precipitate all the iron when the furnace product is dissolved in boiling water. The solution is clarified and allowed to cool, and the crystals, after passing through the hydro-extractor, are ready for packing. By this means also the crystals can be produced in a shorter time, about six days being the average required.

Strontium dioxide, SrO_2, is formed as a hydrate when a solution of strontium hydrate is mixed with one of hydrogen peroxide, shining scales of the composition $SrO_2 + 8H_2O$ being deposited. When heated to 130°, or even in dry air at the ordinary temperature, it gives off water, and the peroxide is left in the form of a white powder. On heating this powder to redness, oxygen is evolved without fusion, strontium monoxide remaining.

Strontium chloride, $SrCl_2$, is formed directly by the combustion of strontium in chlorine, or by heating anhydrous strontia in a stream of chlorine. According to Konigel-Weisberg (B. 12, 511), chlorine has no action on dry $Sr(OH)_2$, but it converts the hydrate $Sr(OH)_2 + 8H_2O$ into chloride and chlorate, a small quantity of hypochlorite being also formed. Strontium chloride is generally obtained from strontianite or celestine. The former, dissolved in hot hydrochloric acid, deposits on cooling long hexagonal deliquescent needles of $SrCl_2 + 6H_2O$ of sp.gr. 1·603, isomorphous with the hydrate of calcium chloride. When heated the crystals lose their water, the white anhydrous salt being left, which fuses at a high temperature, forming a glassy mass of sp.gr. 2·96. According to Mulder, 100 parts of water dissolve 44·2 parts $SrCl_2$ at 0°, 83·1 parts at 60°, and 101·9 parts at 100°. It is also soluble in alcohol.

The anhydrous chloride absorbs dry ammonia, forming a white powder of the composition $SrCl_2.8NH_4$.

Wackenroder (D. P. J. 253, 440) proposes to prepare strontium chloride on the large scale by adding an equivalent of calcium chloride to strontium sulphide obtained by the reduction of celestine, and passing carbon dioxide into the mixture, when sulphuretted hydrogen is given off and the calcium precipitated as carbonate. The filtered solution is then evaporated to the crystallising-point of the strontium chloride.

Mactear (Pat. 1,915, 1886) mixes celestine and calcium chloride with charcoal or other form of carbon and a little limestone or lime, and strongly heats the mixture in a furnace, the waste fire-gases being utilised to dry the calcium chloride. The product, consisting of strontium chloride and calcium sulphide or oxysulphide, yields on lixiviation solutions from which strontium chloride can be crystallised.

Strontium oxychloride. When strontium hydrate is boiled in a concentrated solution of strontium chloride, the liquid, on cooling, deposits nacreous lamellæ of $SrCl_2.SrO + 9H_2O$, easily decomposed by water and alcohol. *In vacuo* this oxychloride loses water, becoming $SrCl_2.SrO + H_2O$ (Andre, C. R. 93, 58).

Strontium bromide, $SrBr_2$, is obtained when strontium is burnt in bromine vapour, or when the carbonate is dissolved in hydrobromic acid. From the solution, on evaporating, long needles of the hydrate $SrBr_2 + 6H_2O$ are obtained. It is readily soluble in water and slightly soluble in alcohol.

Strontium iodide, $SrI_2 + 7H_2O$, is prepared by evaporating a solution of hydriodic acid saturated with strontium hydrate. It crystallises in six-sided plates, very soluble in water. Heated in a closed vessel it may be fused without parting with iodine, but in contact with air iodine fumes are evolved, oxide of strontium being left.

Strontium fluoride, SrF_2, is also similarly obtained by treating the oxide or carbonate with hydrofluoric acid, or by precipitating a soluble strontium salt with sodium fluoride. Strontium fluoride is a white powder insoluble in water.

Strontium carbonate, $SrCO_3$, occurs native as strontianite in rhombic crystals, isomorphous with those of arragonite and witherite. Strontium oxide absorbs CO_2 like CaO when strongly heated to a temperature about 1,050°, becoming incandescent, the luminosity being greater than that of lime. But the normal carbonate is never obtained in this way (Raoult, C. R. 92, 1,110). When a solution of a strontium salt is precipitated by an alkaline carbonate, strontium carbonate is obtained as a white powder of sp.gr. 3·62. It may be obtained crystallised in the form of strontianite by fusing a mixture of KCl,NaCl and the amorphous carbonate, and allowing to cool (Bourgeois, Bl. [2] 37, 447). When gently heated it loses its CO_2, and becomes converted into strontia. A litre of water, according to Fresenius, dissolves 55 milligrams of strontium carbonate. It is still less soluble in aqueous ammonia or ammonium carbonate, but dissolves more readily in ammonium chloride and nitrate. Boiled with ammonium chloride solution it becomes converted into strontium chloride.

Several processes have been devised, in view of the use of strontia in sugar refining, for the production of strontium carbonate on the large scale. Urquhart and Rowell (D. P. J. 1884, 252) treat native sulphate (celestine) with sulphuric acid to remove iron and aluminium, then boil the product with mixed solutions of sodium sulphate and carbonate.

The resulting mixture of strontium sulphate and carbonate is heated in a furnace with excess of Na_2CO_3, and the melt lixiviated, $SrCO_3$ being thus obtained, together with a liquor which is used for the first treatment of fresh celestine.

Mebus and Decastro (D. P. J. 257, 198) digest finely-pulverised $SrSO_4$ with a solution of ammonium carbonate, the decomposition being effected in an apparatus fitted with agitating appliances.

A basic hydrated carbonate of strontium is formed when the dihydrate $Sr(OH)_2 + H_2O$ is exposed to a current of dry CO_2, and the product dried at 145° (Finkener, B. 19, 2,958).

Strontium nitrate, $Sr(NO_3)_2$, may be prepared by dissolving the carbonate in dilute nitric acid. On allowing the hot concentrated solution to evaporate, the anhydrous nitrate separates out in transparent crystals belonging to the regular system, generally in octahedrons modified by faces of the cube. Its sp.gr., according to Schröder, is 2·96. It possesses a cooling taste, and when thrown upon red-hot charcoal deflagrates, burning with a red flame. Owing to the fact that this salt lends itself most readily to the production of red fire, it is much used in pyrotechny.

On cooling a dilute solution of strontium nitrate a hydrate $Sr(NO_3)_2 + 4H_2O$ separates out in large monoclinic prisms, which rapidly effloresce in the air. Strontium nitrate is soluble in about twice its weight of water at 13°, and in an equal weight at 100° (Mulder). It is but slightly soluble in alcohol and almost insoluble in strong nitric acid.

Di-strontium ortho-phosphate, $Sr_2H_2P_2O_8$, or $SrHPO_4$, is obtained by precipitation of solutions of strontium salts with disodium phosphate as a white amorphous powder, insoluble in water but soluble in acids or ammonium salts. It is not decomposed by aqueous solutions of alkalis. After being heated strongly to the fusing-point it exhibits phosphorescence.

According to Kühn, a mixture of di-strontium and mono-strontium phosphates is formed when the strontium salt is incompletely precipitated in the cold by the alkaline phosphate.

Potassium strontium phosphate $KSrPO_4$, and sodium strontium phosphate $NaSrPO_4$, are obtained by ignition of one molecule strontium pyrophosphate with a molecule of potassium or sodium carbonate and extraction with water. They are, however, somewhat readily decomposed by water, the residue being invariably found to contain neutral strontium phosphate. According to Joly (C. R. 104, 905), a molecule of HNa_2PO_4 reacts with one of $SrCl_2$ in three stages. A gelatinous trimetallic phosphate is first formed, which then becomes crystalline, and is afterwards transformed into di-strontium phosphate, the solution becoming acid. The thermometer remains stationary at first, while cubic crystals of $NaSrPO_4 + 9H_2O$ begin to form, almost insoluble in cold water. If the precipitate is allowed to remain in the liquid and phenolphthaleïn added, and then aqueous soda, a white gelatinous precipitate, rapidly crystallising, is formed. When the indicator changes, one equivalent of alkali has been added, and the whole of the strontium is precipitated as $NaSrPO_4 + 9H_2O$.

Strontium pyrophosphate, $Sr_2P_2O_7$, is obtained by precipitation as an amorphous powder, rapidly becoming crystalline when the liquid is kept warm. It is insoluble in acetic but soluble in stronger acids. Heated to 100° the hydrate $Sr_2P_2O_7 + H_2O$ is left, but above that temperature the water is driven off.

On adding strontium nitrate to a boiling solution of sodium pyrophosphate, a precipitate forms which is probably a mixture of strontium pyrophosphate with a double salt.

Di-strontium arsenate, $SrHAsO_4$. When a solution of HNa_2AsO_4 is added to one of $SrCl_2$, a precipitate of $SrNaAsO_4 + H_2O$ is thrown down; when the filtrate from this is evaporated, a white precipitate of the di-strontium salt is obtained (Salkowski). According to Joly (C. R. 104, 905), when one molecule $SrCl_2$, solution is added to one of HNa_2AsO_4 no precipitate is formed, the solution remaining alkaline; but after some time, if the sides of the vessel are rubbed, a crystalline precipitate separates, and the liquid becomes acid. In twenty-four hours large cubic crystals of $NaSrAsO_4 + 9H_2O$ (isomorphous with corresponding phosphate) are deposited. On addition of one equivalent NaOH, the precipitation is complete.

Silicate of strontium. According to Kirwan, equal weights of strontia and silica fuse, with formation of an amber-coloured glass and a black and white enamel. Vauquelin finds that with 3 parts of strontia a solid grey mass is formed, difficultly soluble in water, but readily in dilute acids. According to Kuhlmann, strontium carbonate, digested in solution of silica, is converted into a hydrated silicate of strontium.

Strontium monosulphide, SrS, is prepared by reduction of the sulphate with coal or other form of carbon. It is a white, granular, semi-fused and brittle mass. It is decomposed by treatment with a large quantity of boiling water, with formation of strontium hydrate, which crystallises out on cooling, and strontium sulphydrate, which remains in solution:

$$2SrS + 2H_2O = Sr(OH)_2 + Sr(SH)_2.$$

If a less quantity of water be employed, nearly pure sulphydrate is extracted, while the residue on treatment with more water gives a solution of almost pure hydrate.

The sulphide of strontium obtained by heating 100 parts $SrCO_3$, 30 parts sulphur, and 5 parts arsenious oxide shows a greenish-blue phosphorescence if the carbonate has been prepared from the chloride and ammonium carbonate, but a greenish-yellow if precipitated by sodium carbonate (Verneuil, C. R. 103, 600). According to Becquerel (C. R. 104, 551), the colour of the phosphorescence varies with the temperature. At −20° it is violet-blue, at +40° pale blue, at 90° a greenish yellow, and at 150° orange. The reverse series of colour-changes is noticed as the temperature falls.

Strontium tetrasulphide, SrS_4. When the monosulphide and sulphur are digested in water in the proportion of 1 to 3 molecules, and the solution allowed to evaporate below 17°, a brown syrup is obtained which crystallises at 8° to a mass of the composition $SrS_4 + 6H_2O$. This substance is very hygroscopic, and soluble in alcohol as well as in water. On exposing the solutions to the air, thiosulphate of strontium remains in solution, sulphur and a little $SrCO_3$ being deposited. On heating the syrup to 100°, or concentrating under the air-pump between 20° and 25°, a light-yellow solid of the composition $SrS_4 + 2H_2O$ separates. Heated above 100°, its own water of crystallisation decomposes it. It is insoluble in carbon bisulphide.

When an alcoholic solution of SrS_4 is exposed to air, transparent ruby-red rhombic crystals are formed of the composition $SrO.SrS_4 + 12H_2O$, which are decomposed by water. They are probably identical with Gay-Lussac's disulphide, which he obtained by allowing a solution of strontium sulphide to stand.

Strontium pentasulphide, SrS_5, is obtained when the monosulphide is digested in water with 4 molecules of sulphur, but is only known in solution. On attempting to isolate by evaporation under the air-pump, a mixture of the tetrasulphide and sulphur is obtained (Schöne, P. 117, 56).

Strontium sulphydrate, $Sr(SH)_2$, is readily obtained by saturating strontia water with sulphuretted hydrogen, or by passing sulphuretted hydrogen through water holding strontium sulphide in suspension. Also by dissolving the monosulphide in a small quantity of boiling water, by which it is decomposed into soluble sulphydrate and insoluble hydrate. By evaporating the solution obtained by the first method, Berzelius obtained the sulphydrate in large striated prisms, which on heating melt in their water of crystallisation, then give it off, together with sulphuretted hydrogen, and leave a residue of the monosulphide.

Strontium sulphite, $SrSO_3$. Strontia commences to absorb sulphur dioxide at 230° with production of $SrSO_3$. Strontium sulphite is obtained by double decomposition as a white powder soluble in aqueous sulphurous acid, from which solution the sulphite is again deposited in crystalline grains. The crystals are flat, rectangular tables, which are gradually converted to sulphate on exposure to air.

Strontium sulphate, $SrSO_4$, is found native as celestine in large rhombic crystals and fibrous masses. The name celestine was originally given to the mineral on account of the light-blue tint which it generally possesses. By fusing potassium sulphate with excess of strontium chloride, Manross obtained well-developed artificial crystals of celestine. Sulphuric acid added to the solution of any strontium salt gives a precipitate of sulphate more or less crystalline. According to Haushofer (J. M. 1887, 1, Ref. 15), solutions containing 0·1 grm. $SrCl_2$ in 20–80 c.c. water treated with 1 c.c. concentrated hydrochloric acid, give with dilute sulphuric acid very perfect rhombic crystals. Precipitated strontium sulphate has a sp.gr. of 3·7, and fuses on being strongly heated. It is less soluble in hot than cold water, but is more soluble in acids.

According to Fresenius, one litre of water at ordinary temperature dissolves 0·145 grm. and 0·104 grm. at 100°. This aqueous solution at once gives a turbidity with solutions of barium salts. Strontium sulphate dissolves to a considerable extent in a solution of common salt and other saline solutions, but the presence of sulphates or dilute sulphuric acid diminishes the solubility. Unlike barium sulphate, strontium sulphate is completely converted to carbonate by boiling with solutions of alkaline carbonates.

Strontium sulphate is soluble in hot, strong sulphuric acid, crystals of celestine separating out on cooling. If heated with strong sulphuric acid to 100° and the solution digested with an excess of salt at a still higher temperature, the acid salt, $SrH_2(SO_4)_2$, separates as a crystalline powder, which changes on exposure to moist air to the hydrated salt $SrH_2(SO_4)_2 + H_2O$, forming shining tabular crystals. According to Varenne and Pauleau (C. R. 93, 1016), one grm. of $SrSO_4$ precipitated from the chloride dissolves in 1256 grms. sulphuric acid.

Strontium chromate, $SrCrO_4$, is formed as a lemon-yellow precipitate, composed of slender microscopic needles, when a strong solution of chloride or nitrate of strontium is mixed with one of neutral potassium chromate. After drying over sulphuric acid or at 100° the salt is anhydrous, and remains unaltered on heating. One part of the salt is soluble in 840 parts of water at 16°. It is readily soluble in hydrochloric, nitric, and chromic acids. It dissolves with difficulty in acetic acid, and is insoluble in alcohol. No precipitate is formed in presence of acetic acid if the solution contains for one mol. K_2CrO_4 one mol. $Sr(NO_3)_2$ or acetate and 30 mols. water, or for one mol. $SrCl_2$, 25 mols. H_2O. The separation from barium by means of K_2CrO_4 is, therefore, not complete, some $SrCrO_4$ coming down along with the $BaCrO_4$ (Meschtchersky, Journ. Russ. Chem. Soc. 1882, 219).

Bourgeois (J. M. 1880, 1, Ref. 351) prepared $SrCrO_4$ by heating 2 mols. $SrCl_2$ with 1 mol. K_2CrO_4 and 1 mol. Na_2CO_3 to bright redness. The $SrCrO_4$ thus obtained forms beautiful yellow rhombic lamellæ, cleaving parallel to faces of a rhombic prism, and sparingly soluble in water.

Strontium dichromate, $SrCr_2O_7 + H_2O$, has been obtained by Preis and Rayman (B. 13, 340) by dissolving $SrCrO_4$ in concentrated chromic acid and drying the product at 100°. It consists of readily-soluble dark-red crystals. A second salt, containing $3H_2O$, was obtained in the form of red deliquescent crystals.

Detection and estimation of strontium. Strontium salts colour the flame a characteristic crimson. Examined by the spectroscope, the spectrum is found to consist of a large number of bright lines, of which the orange line $Sr\alpha$, the red lines $Sr\beta$ and $Sr\gamma$, and the blue line $Sr\delta$ are most characteristic. Even in presence of a large quantity of barium salts, this reaction affords a ready means of distinguishing strontium.

In its reactions strontium very much resembles barium. It chiefly differs in forming more soluble salts. Thus the sulphate, chromate, and silico-fluoride are considerably more soluble. Hence dilute solutions are only precipitated after some time by sulphuric acid or soluble sulphates, and a solution of strontium sulphate gives an immediate precipitate with soluble barium salts.

The chromate is very much more soluble, a precipitate of stellar aggregates of needles only forming with strong solutions and in absence of much acetic acid. Strontium sulphate is formed after a time if the solution is dilute, but immedately if strong, on addition of a solution of calcium sulphate to one of a soluble strontium salt, and thus strontium may be distinguished from calcium.

Strontium may be estimated as carbonate by precipitation with ammonium carbonate and ammonia from a hot solution; the carbonate is not decomposed by ignition over an ordinary Bunsen lamp. It may also be estimated as sulphate, the completion of the precipitation being effected by addition of alcohol. This method, of course, can only be used when the original strontium salt is soluble in alcohol.

Atomic weight of strontium. Marignac found that 100 parts of the hydrated chloride

$$SrCl_2 + 6H_2O$$

required 80·998 parts of silver for complete precipitation, and that the same quantity yielded 68·855 parts of strontium sulphate. These numbers give for the atomic weight of strontium 87·2. A. E. T.

STROPHANTHUS. *Kombé Arrow-poison.* The seed of *Strophanthus hispidus* (De Cand.) is used by the natives of Central Africa for the preparation of arrow-poison. A paste is made by crushing the seed with water, and with this the arrow-heads are smeared. Arrows tipped in this way appear to be used both in warfare and in the chase. In the latter case the animal falls quickly, when the flesh immediately around the wound is cut away and the remainder eaten without any injurious effect. Strophanthus arrow-poison is very widely used throughout the whole of Central Africa, specimens having been obtained and sent to Europe from time to time from nearly all parts of the east and west coasts. The plant is a woody climber of the natural order *Apocynaceæ*, which ascends the highest trees and hangs in festoons from one to another. The pods contain one to two hundred seeds, each seed weighing about half-a-grain, and having attached to it a beautiful comose appendage on an extremely brittle stalk. The seed was first examined by T. R. Fraser, of Edinburgh, in 1872, who drew attention to its important physiological action on the movements of the heart, and pointed out that both its physiological and toxic action depends upon the presence of an active constituent to which he gave the name 'strophanthin' (Ph. [3] 3, 523; 19. 660).

There has been some doubt as to the precise botanical origin of the seed of commerce. That examined by Fraser came from the East coast, has a fawn colour, and when viewed in certain positions a greenish-grey appearance. West African seed is dark-brown in colour and smaller. The latter is without doubt derived from *S. hispidus*, and to distinguish the former, which alone is recognised by the Pharmacopœia, it is described as the product of *S. hispidus*, variety *Kombé* (Oliver) (Holmes, Ph. [3] 21, 233; Brit. Pharm. Additions, 1890, 29). V. also Holmes

(Ph. [3] 16, 778; 17, 903); Maisch (Ph. [3] 17, 972); Hanausek (Ph. [3] 17, 972); Blondel (J. Ph. [5] 17, 249, 297, a. 554); Christy (Ph. [3] 20, 318).

In 1877 Hardy and Gallois isolated an active crystalline compound from strophanthus seed which was named 'strophantin,' and which had neither the characters of a glucoside nor those of an alkaloid. An inert base 'ineïne' was also described (C. R. 84, 261; Ph. [3] 7, 756). Fraser, however, finds the active constituent to be a glucoside, which readily breaks up under the influence of dilute acids into an easily-crystallisable neutral compound and glucose. The glucoside is *strophanthin*, and the neutral compound produced by its decomposition *strophanthidin*, the latter probably identical with the 'strophantin' of Hardy and Gallois. Both these compounds are toxic and bitter, and have similar physiological action. The seed also contains a large proportion of *fixed oil*, and an acid forming an insoluble lead salt, *kombic acid*; but the presence of the alkaloid 'ineïne' has not been confirmed (Ph. [3] 18, 69; 20, 328).

A specimen of seed examined by Fraser lost at 100° 6·7 p.c. of water, and the residue yielded successively to petroleum ether 31·81 p.c. of oil; to ether, 0·845 p.c. chiefly resin and chlorophyll; to rectified spirit, 8·94 p.c. of bitter extract; and to water, 9·3 p.c. mostly mucilage and albumen. Burnt, there remained 3·514 p.c. of ash; insoluble undetermined constituents, 38·891 p.c. *Strophanthin* is found in the alcoholic extract. To obtain it a concentrated solution of the extract in water is prepared, and precipitated by a solution of tannin. The precipitate is well washed and mixed with enough moist oxide of lead to combine with the quantity of tannin employed. This mixture is allowed to digest at a low temperature for several days, and when dry is extracted successively with rectified and proof spirit. If any tannin remains in the solution, the lead oxide process has to be repeated. Excess of lead is removed from the alcoholic solutions by a stream of carbonic acid gas passed for two or three days. The solutions are then evaporated to dryness, the residue exhausted with rectified spirit, and the alcoholic solution precipitated by the addition of ether. The more or less crystalline precipitate of crude strophanthin thus obtained is purified by solution in alcohol and evaporation in a vacuum. The yield of strophanthin amounts to 65 p.c. of the alcoholic extract.

Strophanthin, obtained in this way, consists of a colourless opaque brittle mass of microscopic crystalline plates. Larger crystals may be produced by adding ether to an alcoholic solution, and allowing the mixture to stand for several days in a closed vessel. It has the composition $C_{16}H_{26}O_8$. It melts at 173°, but changes colour somewhat at 146°. It is very soluble in water and aqueous alcohol; is less soluble in alcohol, acetone, and amylic alcohol; and is insoluble in ether, chloroform, petroleum ether, and carbon bisulphide. Mineral acids give characteristic colour-reactions with strophanthin. Sulphuric acid in the cold strikes a bright-green colour, which on heating to 43–49° changes to olive, dark-brown, violet, violet-blue, and finally to a violet-black. A 10 p.c. solution of sulphuric acid produces similar changes of colour. Nitric acid gives colour-reactions. Hydrochloric acid dissolves it, forming a pale-yellow solution, changing to brownish-yellow. A 10 p.c. solution of hydrochloric acid forms a colourless solution, which when heated to 46–54° for twenty minutes changes to green and dark-blue, the latter colour remaining for several hours (Fraser). If a trace of strophanthin, dissolved in a drop of water, be mixed with ferric chloride and a drop of sulphuric acid added, a reddish-brown precipitate forms, which either at once or after standing some hours changes to emerald green (Helbing, S. C. I. 1891, 575).

By the action of dilute acids strophanthin or the alcoholic extract of strophanthus yields *glucose* and *strophanthidin*. In one experiment a 3·3 p.c. solution of strophanthin in water was acidulated with sulphuric acid kept at 100° for half-an-hour; when, on cooling, crystals of strophanthidin made their appearance, and when separated and weighed represented 36·2 p.c. of the strophanthin taken. The glucose formed represented in the same manner 27·5 p.c. Strophanthidin is slightly soluble in cold water, more soluble in chloroform and in cold aqueous alcohol. It is freely soluble in aqueous alcohol on warming. It is not a glucoside (Fraser).

Kombic acid has not been isolated in a definite condition. The *oil* extracted by petroleum ether does not appear, when properly washed, to possess any physiological activity. It varies in colour from pale yellow to green and brown, and in sp.gr. from 0·975 to 0·927 (Fraser). See also Elborne (Ph. [3] 17, 743; 18, 219); Helbing (Ph. [3] 17, 747 a. 924); Gerrard (Ph. [3] 17, 923); Merck (Ph. [3] 18, 72); Adrian a. Bardet (Ph. [3] 18, 539); Castillon (J. Ph. [5] 17, 334; Fischer (Ph. Post, 20, 489).

The arrow-poison of the Somalis, 'ouabaïo,' the botanical origin of which is not known with certainty, contains a compound, *ouabaïn*, which is nearly related to strophanthin or strophanthidin. This compound is now prepared from a variety of strophanthus seeds, known in the market by the unscientific name of 'strophanthus glabrus' (Holmes, Ph. [3] 21, 234; Arnaud, C. R. 106, 1011; 107, 1162; Cathelineau, J. Ph. [5] 20, 436). A. S.

STRYCHNINE *v.* Vegeto-alkaloids.

STYPHNIC ACID *v.* Phenol and its homologues.

STYRACIN *v. Storax*, art. Balsams.

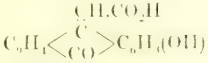
STYROGALLOL. By the condensation of gallic acid with cinnamic acid by means of H_2SO_4, Jacobsen and Julius have obtained a new dye-stuff, *styrogallol*, which presents a great similarity to the colouring matters of the hydroxyanthraquinone group.

Kostanecki has previously shown that in the analogous condensation of the hydroxy-benzoic acids with benzoic acid only those hydroxybenzoic acids which have at least one OH group in the *meta*- position to the CO_2H are capable of forming hydroxyanthraquinones. In a similar manner the condensation with cinnamic acid also proves to be general for all such metahydroxy- derivatives of benzoic acid. The products are analogues of styrogallol, and are formed according to the general equation—

$$C_6H_{5-x}(OH)_x = CO_2H + C_6H_5.C_2H_2.CO_2H$$
$$= C_{16}H_8O_{2+x} + 2H_2O + H_2.$$

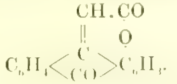
The simplest of these compounds, $C_{16}H_8O_3$, is obtained from *m*-hydroxy-benzoic acid and cinnamic acid. It is insoluble in alkalis, in which it differs from its dihydroxy- derivative, styrogallol.

The first step in the condensation is probably the formation of the hydroxy-acid



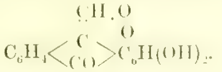
$$\begin{array}{c}CH.CO_2H\\ \|\\ C_6H_4<\begin{matrix}C\\CO\end{matrix}>C_6H_3(OH),\end{array}$$

which then gives the lactone



$$\begin{array}{c}CH.CO\\ \|\quad O\\ C_6H_4<\begin{matrix}C\\CO\end{matrix}>C_6H_3.\end{array}$$

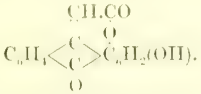
Styrogallol, being the dihydroxy- derivative of this, would therefore have the formula:



$$\begin{array}{c}CH.O\\ \quad O\\ C_6H_4<\begin{matrix}C\\CO\end{matrix}>C_6H(OH)_2.\end{array}$$

The compound $C_{16}H_8O_3$ is prepared by heating molecular proportions of *m*-hydroxybenzoic acid and cinnamic acid with an excess of concentrated H_2SO_4 upon the water-bath for some hours. The product is purified by precipitation with dilute ammonia, extraction with benzene, and sublimation or crystallisation from acetic acid. It is very similar in appearance to anthraquinone, subliming in large glistening yellow needles, and crystallising from acetic acid in small yellowish needles, which melt at 260°. It is slightly soluble in alcohol, with an eosin-like fluorescence. The solution in H_2SO_4 is yellow, with a green fluorescence. It is insoluble in alkalis, but dissolves, on boiling, to a yellow solution, with green fluorescence, probably forming a salt of the corresponding acid.

By heating cinnamic acid and the symmetric dihydroxy-benzoic acid (equal molecules) with concentrated H_2SO_4 at 60°, the compound $C_{16}H_8O_4$ is very readily formed. This is the *m*-hydroxy- derivative of the preceding body, and probably has the constitution:



$$\begin{array}{c}CH.CO\\ \quad O\\ C_6H_4<\begin{matrix}C\\C\end{matrix}>C_6H_2(OH).\\ O\end{array}$$

It sublimes and crystallises from acetic acid in yellow needles, which melt at 325°. It dissolves in alkalis or concentrated H_2SO_4 with a yellow colour, but is insoluble in most other solvents. In cold baryta-water it dissolves, but on boiling forms the insoluble barium salt of the corresponding acid. Its acetyl- derivative forms yellow felted needles, of melting-point 255°.

The analogy of styrogallol with alizarin in its attraction for oxide mordants is no doubt due to its containing two OH groups in the ortho- position to each other. The fact that these hydroxyl groups are not in the same position with reference to the CO group as in alizarin

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OH)_2\ CO:OH:OH = 1:2:3$$

makes it probable that the corresponding dihydroxyanthraquinone

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OH)_2,[CO:OH:OH = 1:3:4]$$

when prepared will be found to have similar mordant dyeing powers (H. v. Kostanecki, B. 20, 3137–3145; S. C. I. vii. 117).

STYROL *v. Storax*, art. Balsams.

SUBERIC ACID $C_6H_{12}(CO_2H)_2$. A dibasic acid, first obtained by Brugnatelli, in 1787, by heating cork with nitric acid. Is also obtained by heating paper, linen, and various fats with nitric acid. Best prepared by heating castor oil with nitric acid, sp.gr. 1·25, until no further evolution of red fumes occurs, distilling the mass with frequent addition of water to remove oxanthylic acid, and separating the mixed azilaic and suberic acids by means of ether (Grote, A. 130, 208; Dale, C. J. [2] 2, 258). Sparingly soluble in cold water, more readily in hot water; m.p. 140°, b.p. about 300°. May be sublimed. On distilling with lime it yields *hexane* C_6H_{14}, and *suberone* $C_7H_{12}O$; b.p. 179–181° (Boussingault, A. 19, 308; Tilley, C. J. 1, 1; Dale and Schorlemmer, C. J. 1879, 1, 686).

SUBLIMATION. The passage of a stable substance, when heated, into the state of vapour may take place in one of three ways:—

1. The substance is liquid under ordinary conditions; it boils at a definite temperature, depending on the pressure.
2. The substance is solid; when heated it melts at a definite temperature, and when more strongly heated it boils like an ordinary liquid.
3. The substance is solid; when heated it does not melt, but passes directly from the solid state to that of vapour at a definite temperature depending on the pressure.

Similarly in the condensation of vapour we may have (1) liquefaction; (2) liquefaction and subsequent solidification; (3) direct passage from the gaseous to the solid state.

The term *distillation* is applied to vaporisation and subsequent condensation of the first kind, *sublimation* to the corresponding changes of the third order.

Vaporisation and condensation of the second kind should be included under the term *distillation*, since it is really liquid which is converted into vapour, and which, as a rule, is first formed in the process of condensation. The term sublimation is, however, not unfrequently employed in the case of substances whose melting-points are high or are not far removed from their boiling-points, and, indeed, if the application of the term were strictly limited to changes of the third class it would not be very frequently employed in practical chemistry.

As a matter of fact, the majority of substances may undergo either distillation or sublimation, according to the pressure under which the vaporisation and condensation take place. This may be best understood by means of the diagram (fig. 1), in which temperatures are measured as ordinates and pressures as abscissæ.

The curve A B represents the boiling-points of a substance, the curve C A its subliming-points, and the curve A D its melting-points under varying pressures. The boiling and subliming-points vary greatly with alteration of pressure, the melting-points to so slight an extent that the curve A D, drawn to true scale for any substance, could not be distinguished in such a diagram from a straight horizontal line.

All three curves intersect each other at A, the *triple point* of Prof. Jas. Thomson. The temperature at A, measured vertically from the horizontal axis O X, gives the melting-point of the substance under the pressure represented by the horizontal distance of A from the vertical axis O X; it is practically the same as the melting-point under atmospheric pressure—generally a small fraction of a degree lower.

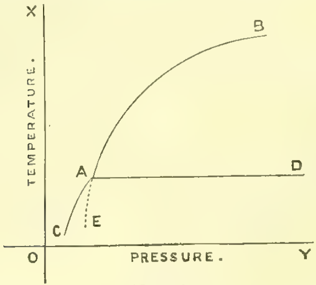


Fig. 1.

If a solid substance is heated under pressures greater than the *triple-point pressure*, its temperature will rise until the melting-point is reached; then, after fusion, the temperature will again rise until the liquid reaches its boiling-point. The melting- and boiling-points under any given pressure are indicated by the intersection of a vertical line representing that pressure with the curves A D and A B.

If, however, the pressure is lower than the triple-point pressure, the substance cannot, under ordinary circumstances, exist in the liquid state at all, and when heated it sublimes without previous fusion at a temperature given by the intersection of the vertical line of constant pressure with the curve C A. (It is, however, possible to cool a liquid below its freezing-point without solidification taking place, and it may, indeed, be made to boil below its freezing-point. This is indicated by the dotted line A E, which is simply a continuation of the curve B A.)

The pressure at the triple point varies very greatly for different substances, but in the vast majority of cases it is far below the atmospheric pressure. Hence under ordinary conditions true sublimation rarely takes place.

The following table gives the melting-points, the boiling-points under normal pressure, and the triple-point pressures of a few substances; complete data have been obtained in only a limited number of cases :—

Substance	Melting-point—degs.	Boiling-point -degs.	Triple-point pressure
Water	0	100	4·6 mm.
Acetic acid	16·4	118·5	9·45 ,,
Benzene	5-6	80·2	35·9 ,,
Bromine	−7·1	58·7	44·5 ,,
Nitrogen	−214	−193·1	60 ,,
Iodine	114·3	184·3	91 ,,
Camphor	180	204	380 ,,
Mercuric chloride . . .	288	303	554 ,,
Carbon hexachloride . . .	188 (about)	188 (about)	1 atm.
Arsenic trioxide	200 (about)	?	a little above 1 atm.
Aluminium chloride . . .	180–185	?	a little above 1 atm.
Arsenic	500 (above)	?	above 1 atm.
Carbon dioxide	−57 (about)	−78·2	about 5·3 atm.

Some other compounds—such as mercurous chloride and indium trichloride—sublime without fusion, but exact data are wanting.

It will be seen from the table that the triple-point pressure of carbon dioxide is over five atmospheres, hence when the liquid is allowed to escape from a steel cylinder in which it has been stored under pressure, any of it that escapes vaporisation at once solidifies and cannot be melted in an open vessel, but passes directly into the gaseous state.

Arsenic and arsenious oxide also sublime when heated under atmospheric pressure, and carbon hexachloride sublimes if the pressure be very slightly lowered, but melts and distils if the pressure be slightly raised. Water again cannot exist as a stable liquid under a pressure lower than 4·6 mm. Below this pressure, ice, when heated, sublimes without melting.

The curve C A represents not only the subliming-points of a solid substance under varying pressures, but also the vapour pressures of the substance at varying temperatures (Ramsay a. Young, Ph. 1884, pt. 1, p. 37), just as the curve A B represents both the boiling-points and the vapour pressures of the substance in the liquid state; hence the relation of the subliming-point of a solid to the pressure may be defined in precisely the same way as that of the boiling-point of a liquid. The ordinary definition of the 'boiling-point' (a liquid boils when its vapour pressure is equal to the superincumbent atmospheric pressure) is, however, to some extent misleading.

There is, in the first place, perhaps some ambiguity about the terms 'boiling-point' and a 'boiling' liquid. It is true that when a liquid is described as boiling, the impression conveyed is that the liquid is in a state of ebullition, but the 'boiling-point' is certainly not the temperature of ebullition. What is called the 'boiling-point' of a liquid is usually determined by placing a thermometer in the vapour over the liquid, care being taken that the thermometer bulb is always moistened by condensed liquid. It is, in fact, the condensing-point of the vapour that is directly measured.

On the other hand, in order that a bubble of vapour may form below the liquid, not only has the pressure of vapour or air over the liquid to be overcome, but also that of the column of liquid over the point where the bubble forms, and, lastly, the adhesion of the liquid to the solid surface (or possibly the cohesion of the liquid itself). In the case of a very clean smooth vessel, and a liquid very free from dissolved air, this last factor becomes very important, and the ebullition-point may be considerably higher than the 'boiling-point.' Under the most favourable condition it is somewhat higher (Regnault, 'Relation des Expériences,' 1847, pp. 525 529).

The boiling-point of a liquid is, in fact, not its ebullition-point—which does not depend solely on the pressure—but it is *the highest temperature attainable by the liquid under a given pressure when evaporating with a perfectly free surface, and when heat is received from outwards towards the surface.* It is only under these conditions, where ebullition is obviously impossible, that the boiling-point can be accurately determined by measuring the temperature of the liquid itself (Ramsay a. Young, C. J. 47, 42).

In the case of sublimation this difficulty does not occur, for anything analogous to ebullition is impossible, and since the solid can only be in partial contact with the vessel containing it there is practically always a free surface for evaporation.

The ordinary definition of the 'boiling-point' of a liquid takes also no account of the fact that a law analogous to Dalton's law of partial pressures holds good for distillation and sublimation.

That this is the case is proved by the behaviour of two non-miscible liquids when distilled together (vol. i. p. 691). It is found that the boiling-point and the composition of the mixed vapour are independent of the relative quantities of the two liquids present, and that the 'boiling-point' is the same as that of either liquid when distilled alone under a pressure equal to its partial pressure in the mixed vapour. Hence, as the pressure of the vapour of the one liquid is without influence on the 'boiling-point' of the other, it might be inferred that the pressure of an indifferent gas, such as the air, would be without influence on the 'boiling-point' of a liquid or on the subliming point of a solid. This is, in fact, the case, and it is really not the pressure of the atmospheric air, but that of the vapour itself in contact with the liquid or solid, that influences the 'boiling-' or subliming-point.

In ordinary cases of distillation or sublimation the vapour of the substance completely expels the air from the flask or retort; hence the substance is surrounded by its own vapour at the same pressure as that of the external atmosphere, and the 'boiling-' or subliming-point does depend—though indirectly—on the atmospheric pressure.

But if the substance be made to vaporise in the open air, or in such a manner that the rapid diffusion of the vapour prevents the complete expulsion of the air from the immediate neighbourhood of the substance, then the 'boiling-' or subliming-point does not depend on the atmospheric pressure.

Thus water, when distilled in the ordinary way under a pressure of 15 mm., boils at about 18°C., but Schrötter observed in 1853 (A. 88, 188) that when some water was placed on a shallow clock glass, supported by a short tripod on a second clock glass, in a bell-jar over sulphuric acid, the temperature fell to −3° when the pressure was reduced to 15 mm. More rapid diffusion and removal of vapour was effected by suspending in the bell-jar a thermometer the bulb of which was covered with a sponge soaked in water; in this case, under a pressure of 40 mm., at which the 'boiling-point' of water under ordinary conditions is 34°, the temperature fell to −10°.

The following experiments afford a still more striking proof of the correctness of the statement that the 'boiling-point' does not necessarily depend on the atmospheric pressure. A copper air-bath was heated to 205° and a thermometer, the bulb of which was covered with cotton wool and moistened with boiling water, was suspended in the bath through an opening at the top. The pressure of the atmosphere was 748 mm., and the water on the cotton wool was in a strongly-heated chamber, yet the temperature, instead of remaining at nearly 100°, fell to 66°, and remained constant at this point while the water rapidly evaporated. A second experiment was carried out under the same conditions, except that steam was introduced, so as to replace the air as completely as possible by aqueous vapour. The temperature of the bath was in this case 195°, and the steam was passed into it after the temperature of the water on the thermometer bulb had fallen to 69°; the result was an immediate rise of temperature, the highest point reached being 99°. A fall of temperature to 80° was again observed on allowing some of the steam to escape.

In these cases the 'boiling-point' certainly does not depend on the pressure of the surrounding atmosphere, and in all probability the observation that the temperature of a drop of water in the spheroidal state does not reach 100° (under normal atmospheric pressure) may be explained in the same way, the vapour round the drop of water being always diluted with a certain amount of air. Again, by passing a current of air through water or any other liquid boiling in an ordinary distillation bulb, the vapour above the liquid becomes diluted, and the result is an immediate fall in temperature, both of the liquid and of the vapour, although the liquid continues to distil rapidly, and this is the case even when heated air is introduced.

Thus by bringing about admixture of air with the vapour surrounding a vaporising substance the same effect is produced as by reducing the pressure in an ordinary distillation bulb, and in this way, in certain cases, the partial pressure of the vapour may be reduced below the triple point pressure, so that the substance which in a bulb or test-tube would melt first and then boil, will under these circumstances sublime at a temperature below the melting-point. If the bulb of a thermometer, by repeated immersion in melted camphor, be completely covered by the solid substance, and if the thermometer be then suspended in a strongly-heated air-bath through which a moderate current of air is passing, the camphor will not melt, but will sublime at a temperature lower than its melting-point, although the total pressure is far above the triple-point pressure of camphor.

The slow volatilisation of camphor, iodine, snow, and other substances is to be explained in precisely the same way, vaporisation always taking place when the partial pressure of the vapour in the surrounding air is less than the vapour pressure of the solid substance.

Again, if the vapour of a substance which is solid at the ordinary temperature condense in the narrow neck of a retort or distillation bulb, the liquid state is first as a rule assumed, and solidification afterwards takes place; but if the same vapour be allowed to diffuse into the air, or if by any means sufficient air be mixed with it before condensation occurs, it frequently happens that the solid state is at once assumed without intermediate passage through the liquid state. This direct passage from the gaseous to the solid state must, in fact, occur if by admixture with any indifferent gas the partial pressure of the heated vapour falls below the triple-point pressure before the temperature falls sufficiently for condensation to take place.

Thus on boiling sulphur in an ordinary retort, while the vapour is rising and before the air has been expelled, the formation of small quantities of flowers of sulphur is always to be observed above the vapour; but when the air has been expelled and the sulphur vapour condenses in the neck of the retort, liquid is formed. When, however, as in the formation of flowers of sulphur on the large scale (refer to diagram under SULPHUR), the heated vapour is passed into a large chamber containing air, direct condensation to the solid state occurs until the temperature of the chamber reaches the point at which the partial pressure of the sulphur vapour is higher than the triple-point pressure, when liquefaction takes place.

The phenomenon is still more readily observed in the case of camphor, iodine, and other substances, the triple-point pressures of which are relatively high. Thus if we heat one of these substances in a porcelain basin and hold a cold glass funnel or a glass plate over it, the substance melts and boils in the basin, but condenses as a solid on the funnel or plate. The heavy vapour collects in the basin, so that its partial pressure in the atmosphere surrounding the substance soon rises above the triple-point pressure, when fusion takes place; but before reaching the cold glass surface the hot vapour becomes so diluted with air that the partial pressure falls below the triple-point pressure, so that when condensation takes place the solid state is at once assumed. In the purification of crude anthracene by passing steam, heated to about 230°, over the melted substance, and condensing the vapour in a chamber by jets of cold water, the steam acts as an indifferent gas, and in all probability the partial pressure of the anthracene vapour is far below the triple-point pressure when condensation takes place.

So also when condensation of moisture from the atmosphere occurs at a temperature below 0°, and when the partial pressure of the aqueous vapour is necessarily lower than 4·6 mm., there must be direct passage from the gaseous to the solid state, and the light crystalline snow flakes present all the appearance of having been formed in this way.

Although the process of sublimation is in theory quite analogous to that of distillation, yet the apparatus employed for distillation is unsuited for sublimation, for the narrow condensing tubes would rapidly become blocked by the solid sublimate. In cases of true sublimation, therefore, and also in the distillation of liquids with high solidifying points—such as anthracene, camphor, iodine, &c.—the condensing tube must be wide and comparatively short, as in the Silesian subliming pots for arsenic trioxide (vol. i. p. 200, fig. 8) and in the condensers employed for the manufacture of iodine (vol. ii. p. 342).

The condensing tube may, indeed, be replaced by a simple flat or concave cover over the subliming pot, as in the case of ammonium chloride (fig. 2).

The ammonium chloride is heated in the pots, and condenses in the solid state on the iron covers.

(It is true that in this case the process is not one of simple sublimation, since the vapour does not consist of ammonium chloride, but of a mixture of ammonia and hydrogen chloride; there is really dissociation and recombination instead of vaporisation and condensation, but practically the process is the same as that of sublimation.)

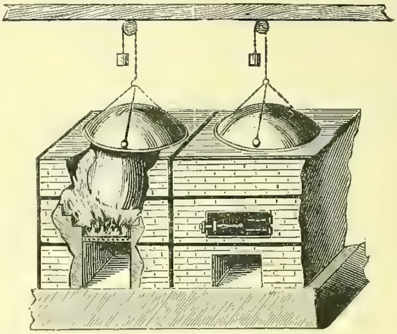


FIG. 2.

It frequently happens that when direct condensation to the solid state takes place, the substance assumes the form of a fine light crystalline powder, or of feathery flakes which are easily carried about by currents of air; hence longer flues or a succession of condensing chambers are required to prevent loss of substance. This is especially the case with such poisonous substances as arsenic or arsenic trioxide, and the condensing tubes attached to the Silesian subliming pots already referred to are supplemented by condensing chambers.

If the sublimation does not take place from a retort or pot, but from a furnace through which the hot gases pass as well as the vapour of the subliming substance, the light sublimate is very liable to be carried away, and the flues must be very long or the chambers very numerous (*v.* ARSENIC TRIOXIDE, vol. i. p. 199, figs. 5, 6, 7). S. Y.

SUCCINIC ACID *v.* RESINS.

SUCCINITE. An amber-coloured variety of lime-garnet. Breithaupt's name for amber.

SUCCISTERENE *v.* RESINS.

SUCROSE. Syn. with Cane Sugar.

SUET. The solid fat of sheep and oxen. Mutton suet is more solid than beef suet, and consists mainly of stearin, together with palmitin and small quantities of olein and hircin; m.p. 50° (Arzbächer). Beef suet contains more stearin than human fat, more palmitin than mutton suet, and about the same quantity of olein; m.p. 47° (Arzbächer, W.).

SUGAR (Fr. *sucre*; Germ. *zucker*) is the generic name for a group of bodies belonging to the class of compounds known as carbohydrates. All carbohydrates contain either 6, or a multiple of 6, atoms of carbon united with hydrogen and oxygen, the two latter in the proportion to form water. The members of the sugar group are mostly possessed of a more or less sweet taste, and several of them are of great value as articles of food, although by themselves, being destitute of nitrogen and various other zootic elements, they are incapable of supporting life for any considerable time. Some bodies possessed of a sweet taste, such as the so-called saccharine, differ widely in composition from true sugars, and are not possessed of any nutritive value. The following table gives the names of the most important members of the sugar group, and also indicates their respective action in causing the plane of polarised light to turn to the right (+), or to left (−).

The Sugar Group.

Glucoses, $C_6H_{12}O_6$.
+ Dextrose, or grape sugar.
− Laevulose, or fruit sugar.
+ Arabinose.
+ Galactose.
+ Eucalyn.
− Sorbin.
Dambose.
Scyllite.
Inosite.

Saccharoses, $C_{12}H_{22}O_{11}$.
+ Saccharose, or cane sugar.
+ Milk sugar, or lactose.
+ Melezitose.
+ Melitose.
+ Trehalose.
+ Maltose.

The limits of the present article will only allow us to give a concise account of the manufacture and refining of ordinary sugar (commonly known as cane sugar), including its mode of production from the sugar-cane, the Sorghum plant, beetroot, &c.

Cane sugar is obtained from the sugar cane (*Saccharum officinarum*); the Sorghum (*Sorghum saccharatum*); the palm ([illegible] and *Saguerus sacc*[illegible]); the maple (*A*[illegible] *saccharinus*); and the beet (*Beta vulgaris*). The sugar-cane has been employed for the production of sugar from an early period, and descriptions exist of the mode of using it as far back as the time of the Crusades, when it was grown in Syria. From thence its cultivation spread to Sicily and to other parts of the southern coast of Europe, next to Madeira and the Canary Islands, and later on (about A.D. 1500) to the West Indies. In 1747, a German chemist, named Margraf, detected the presence of sugar in beetroot and other similar roots, and his pupil F. K. Achard established in 1769 the first beetroot sugar works in Germany, but it was not till 1796 that sugar was made from beetroot on a large manufacturing scale. Since then the industry has increased to a wonderful extent, and the present annual production of beetroot sugar in Europe equals 3,695,000 tons.

Sugar is a crystallisable solid with a characteristic sweet taste, soluble in about half its own weight of cold water, forming a viscid liquid of 1·333 sp.gr.; in hot water it is soluble to a far greater extent. The specific gravity of sugar is 1·593, and its percentage composition is:

Carbon	42·11
Hydrogen	6·43
Oxygen	51·46
	100·00

The following table gives the degree of Baumé's hydrometer, and also the specific gravity of solutions containing various percentages of sugar:

Total showing the relation of percentages, specific gravities, and degrees Baumé in sugar solutions.

Per-cent. of sugar	Specific gravity	Degree Baumé	Per-cent. of sugar	Specific gravity	Degree Baumé
1	1·0038	0·55	44	1·2003	24·0
2	1·0077	1·1	45	1·2056	24·6
3	1·0117	1·7	46	1·2110	25·1
4	1·0157	2·2	47	1·2163	25·6
5	1·0197	2·8	48	1·2218	26·1
6	1·0237	3·3	49	1·2272	26·7
7	1·0277	3·9	50	1·2327	27·2
8	1·0318	4·4	51	1·2383	27·7
9	1·0359	5·0	52	1·2439	28·2
10	1·0401	5·55	53	1·2495	28·75
11	1·0443	6·1	54	1·2551	29·3
12	1·0485	6·7	55	1·2608	29·8
13	1·0527	7·2	56	1·2665	30·3
14	1·0570	7·8	57	1·2723	30·8
15	1·0613	8·3	58	1·2781	31·3
16	1·0655	8·9	59	1·2840	31·85
17	1·0700	9·4	60	1·2898	32·4
18	1·0744	10·0	61	1·2958	32·9
19	1·0788	10·5	62	1·3017	33·4
20	1·0832	11·1	63	1·3077	33·9
21	1·0877	11·6	64	1·3138	34·4
22	1·0923	12·2	65	1·3198	34·9
23	1·0968	12·7	66	1·3260	35·4
24	1·1014	13·3	67	1·3322	35·9
25	1·1060	13·8	68	1·3384	36·4
26	1·1107	14·35	69	1·3446	36·9
27	1·1154	14·9	70	1·3509	37·4
28	1·1201	15·4	71	1·3572	37·9
29	1·1248	16·0	72	1·3635	38·3
30	1·1296	16·5	73	1·3699	38·8
31	1·1344	17 1	74	1·3764	39·3
32	1·1393	17·6	75	1·3828	39·8
33	1·1442	18·15	76	1·3894	40·3
34	1·1491	18·7	77	1·3959	40·8
35	1·1541	19·2	78	1·4025	41·3
36	1·1591	19·8	79	1·4092	41·8
37	1·1641	20·3	80	1·4158	42·2
38	1·1692	20·8	81	1·4226	42·7
39	1·1743	21·4	82	1·4293	43·2
40	1·1794	21·9	83	1·4361	43·7
41	1·1846	22·4	84	1·4430	44·2
42	1·1898	23·0	85	1·4498	44·6
43	1·1950	23·5	86	1·4568	45·1

If a sugar solution be very slowly evaporated, large crystals of 'sugar-candy' are produced, and to assist in the formation of these it is usual to have threads dipping into the syrup, so to act as nuclei.

When pure sugar is heated till it melts, it forms on cooling an amorphous mass known as 'barley sugar.'

If heated to a higher temperature, the sugar is decomposed, forming a dark-coloured mixture of various bodies, termed 'caramel.'

Whether prepared from the sugar-cane or the beetroot, the sugar obtained is, when thoroughly purified, to all intents and purposes identically the same substance.

Sugar unites with various metallic oxides, forming the so-called sucrates. Of these the most important are the sucrates of lime, strontia, and baryta. Sugar also forms compounds with chloride of sodium and many other substances.

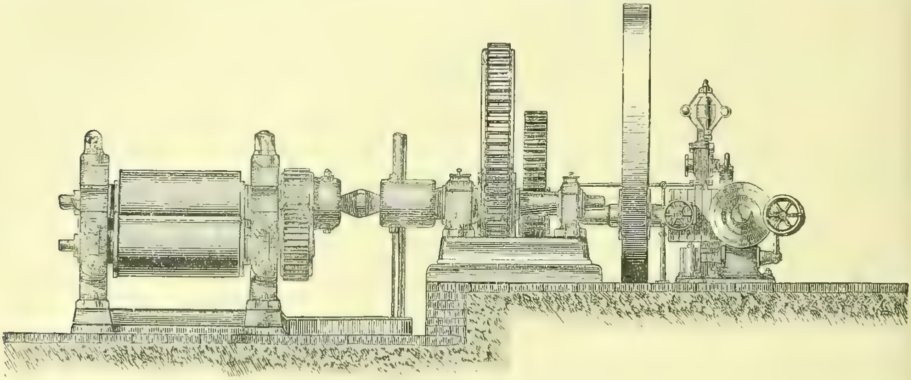


Fig. 1.—Cane Mill (Elevation).

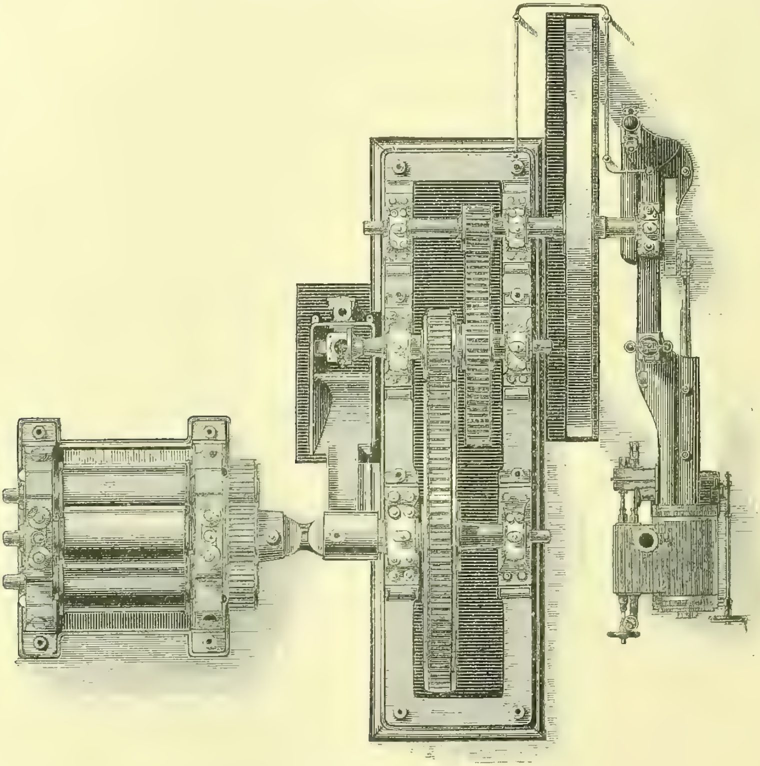


Fig. 2.—Cane Mill (Plan).

Cane sugar manufacture. The sugar-cane flourishes best in a warm, moist climate with moderate intervals of hot dry weather.

The following analyses will give a good idea of the general composition of the sugar-cane, and of the juice obtained therefrom :—

1. *Entire cane.*

Water	71·04
Sugar	18·02
Cellulose	9·56
Albuminous matter	0·55
Fatty and colouring matter	0·35
Salts soluble in water	0·12
Salts insoluble in water	0·16
Silica	0·20
	100·00

2. *Juice of cane.*

Crystallisable sugar	19·64
Uncrystallisable sugar	0·30
Ash	0·25
Water	79·44
Organic matter, &c.	0·37
	100·00

The quantity of cane grown per acre weighs from 30 to 40 tons, so that with 18 p.c. of sugar the crop of a single acre would contain from 5 to 6 tons of sugar. However, 18 p.c. is rather high, and in wet seasons the juice may not contain more than an average of 15 to 16 p.c. for a general crop consisting partly of plant-canes and partly of first or second rattoons or offshoots.

This would still give from 4 to 6 tons of sugar per acre, but, unfortunately, planters seldom make more than 2 to 3 tons per acre, as a large quantity of sugar remains either in the 'megass' or 'begass,' as the refuse cane is termed, or is lost in the process of manufacture. The sugar-cane contains about 88 p.c. of juice, of which the best mills generally express only 60 to 65 p.c.; thus more than 20 p.c. of juice is left in the megass, representing about 4 p.c. of sugar.

The canes are cut when ripe, and conveyed to the mill, and then crushed between rollers, which squeeze out the juice.

The mills usually have three rollers arranged one above the other two, as shown in fig. 2. The canes are fed through the top and one of the bottom rollers, and then are caused to pass between the top and the second bottom roller, so that they are twice crushed. The juice flows into a trough under the rollers, and the begass is carried away. The begass is sometimes moistened with water and again passed through another mill, and by this means an additional amount of sugar is obtained. The begass is employed as fuel.

The juice thus obtained contains pieces of broken cane and other impurities, and these are got rid of by means of wire screens, which can be easily removed and cleaned. The screens are sometimes made of endless-wire gauze passing over rollers, and having a self-cleaning arrangement attached to them. The juice is very liable to undergo fermentation, and to prevent this it is neutralised by lime, and subjected to the action of sulphurous acid gas either before or after such neutralisation. The method of using the sulphurous acid before the lime, which was invented by Colonel Stewart, is mostly employed. The juice is next passed into the 'clarifiers,' where the temperature is raised by the direct heat of a fire, or by steam, to about 170° to 180°F., when defecation takes place, and on the heat being removed the impurities separate as scum and sediment. The 'tempering,' as it is called, or addition of lime to the cane juice, is often made in the clarifiers, the temperature being first raised to 130 F.

After remaining at rest for some time, the clear juice is run into the first of a series of evaporating pans called 'teaches,' a set, or battery, of which is shown in figs. 3 and 4, in which it will be noticed that the vessels are set over a flue, at one end of which is a fire. When the juice has been concentrated in the first teach to a certain extent, it is ladled out into the second, and still further evaporated. It is then removed to the third, and lastly, to the smallest teach, commonly called the 'striking-teach,' being the one nearest the fire, and in this it reaches the crystallising point.

The mass is then removed to 'coolers,' in which it is allowed to grain, and is next transferred to casks, or hogsheads, having a number of holes in their lower part, which are temporarily closed by means of plugs. When the mass has solidified, the plugs are removed, and the syrup is allowed to drain off.

A much better method of working is to remove the boiled mass from the striking-teach by means of a dipper-crane, as shown in fig. 3. The dipper consists of a copper pan, in the bottom of which is a valve opening upwards. The dipper is lowered into the semifluid mass, and, when filled, is hoisted up; the crane is then swung round, and on the valve being lifted the contents fall into a trough leading to coolers, or crystallising tanks, also shown in fig. 3. When the crystallisation is complete, the sugar is separated by means of a centrifugal machine.

Sometimes the waste heat escaping from the flue is used for raising steam in a multitubular boiler, and fig. 3 shows an arrangement by means of which this economy can be effected.

A plan now often adopted is to have flat copper pans, heated by steam worms, each succeeding one being placed at a lower level than the previous one, so that the juice flows from the higher to the lower without being ladled. The syrup which drains away from the first crop of sugar is either concentrated to obtain a second crop of lower quality sugar, or it is fermented and made into rum. The residual scum, containing much sugar, is also employed in distillation. The ash left after burning the begass, together with the distillery residue, is used as manure.

These comparatively imperfect processes are being gradually replaced in many of the colonies by improved plans of working, involving the use of vacuum pans in conjunction with centrifugal machines, the use of which has been attended with excellent results. A description of the vacuum pan and centrifugal machine will be found further on under the head of *Refining*. The neutralised cane juice is also sometimes evaporated by means of Fryer's concretor.

In this the clarified juice is rapidly evaporated without being burnt, and is converted into a solid mass, which is easily packed and is not liable to loss by drainage. To accomplish this the clarified juice is first run over a series of shallow trays, A A, in a stream of about half-an-inch deep (see fig. 5). The trays are divided by ribs running from one side nearly to the other, forming a continuous, narrow, winding channel, in traversing which the juice passes several times from side to side of the tray. In the large sizes there are ten of these trays placed end to end, so arranged that the juice can flow freely from one end to the other of the series, or a length of 48 feet, the juice traversing about six times this length in about five minutes.

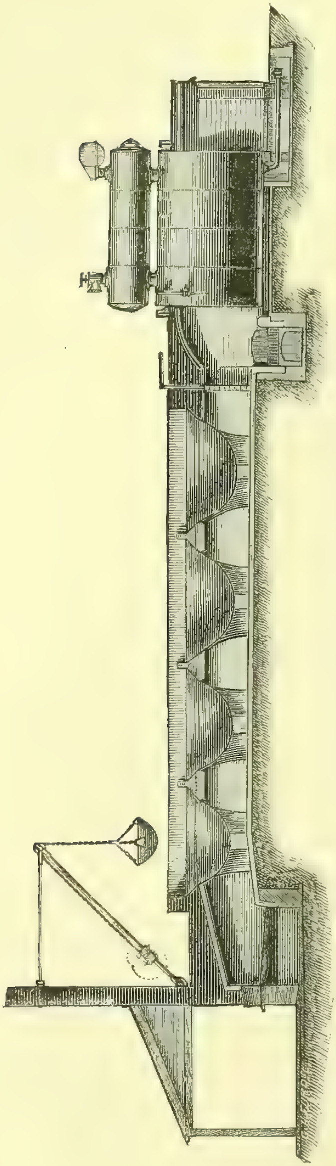


Fig. 3.—Evaporating Pans (Elevation).

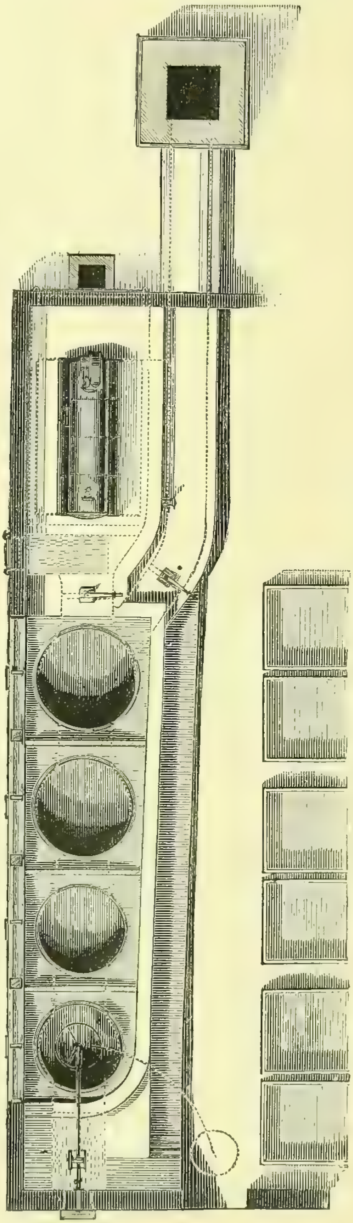


Fig. 4.—Evaporating Pans (Plan).

The heat from the fire B passes under the whole length of the trays, and the juice is in this way brought to a density of from 30° to 40° Baumé. On leaving the trays the juice passes into the revolving cylinder E, in which a very large surface is exposed to the action of a current of heated air drawn through the cylinder by means of a fan, the air being heated by passing through tubes placed in the economiser c. In this cylinder the concentration is continued until the material has attained such a consistency that it drops down in large flakes instead of flowing in a continuous stream. The evaporated mass is then run into casks, and on cooling becomes solid, and ready for shipment. The process takes about half-an-hour, and is a continuous one. No molasses are produced, and the average yield of concrete is about 2 lbs. to the gallon of juice at 10·5° Bé.

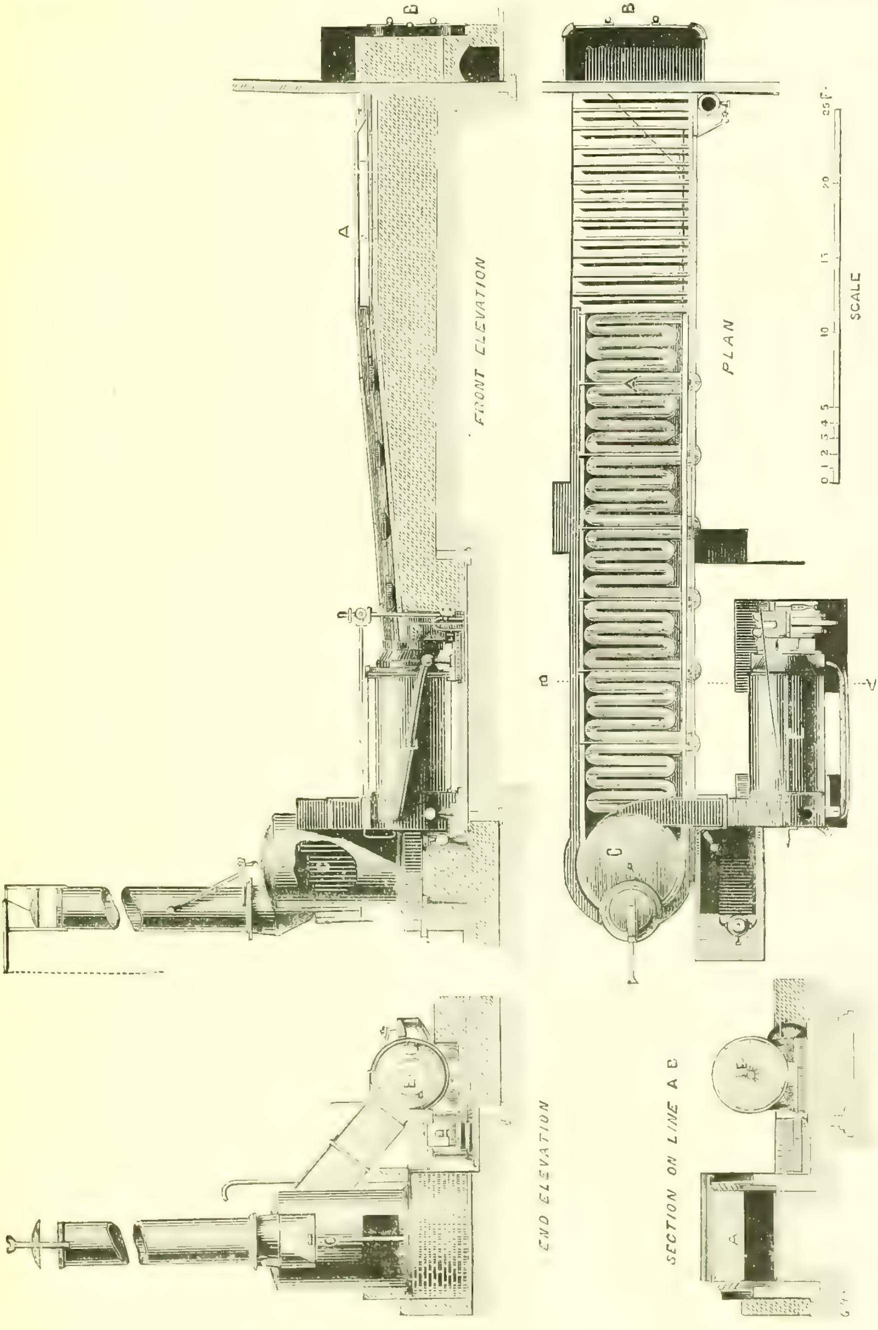


Fig. 5.

The Wetzel evaporator. This apparatus has been largely adopted, and consists of a number of copper pipes, arranged as shown in fig. 6, held together at each end by steam chambers, so constructed that the steam enters one end of the system of pipes and the condensed water flows out of the other whilst it is revolving. The cane juice is run into the pan of the apparatus, and as the pipes revolve they take with them a thin film of the juice, which undergoes partial evaporation and returns to the pan. The operation is continued until the whole contents of the pan are sufficiently evaporated to form a thick semi-solid crystalline mass termed massecuite.

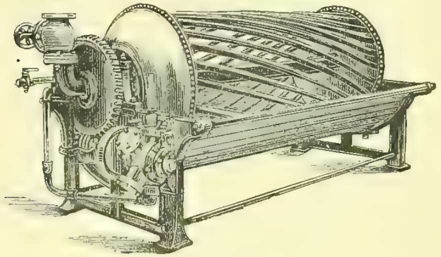


Fig. 6.—Wetzel Evaporator.

Diffusion. In carrying out this process, instead of crushing the sugar-cane it is reduced to small pieces, which are then systematically washed in a way similar to that described further on under the heading *Diffusion process as applied to beetroot sugar.* The juice obtained by the diffusion process is said to be much freer from gummy and albuminous matters than that obtained by the crushing process. The yield of sugar is also considerably increased.

Manufacture of beet sugar. The roots are first cleaned from any adhering earthy matters, and are then trimmed by removing the somewhat green portion at the top. They are next introduced into a rasping apparatus and converted into a fine pulp, which is put into coarse woollen cloths, the juice being extracted by means of a hydraulic press.

The diffusion process. The method usually employed in Germany for extracting the juice from the beetroot is known as the 'Diffusion process.' This plan has been so successful that now but comparatively few sugar factories employ rasps and presses. The diffusion apparatus or batteries may be divided into two classes: first, the ordinary, consisting of a number of cells; and secondly, the continuous, having but one cell. The first may be again divided into 'battery in line' and 'circular battery.' The ordinary battery is usually composed of twelve cells. They are so arranged that, on starting the apparatus, as soon as one cell or diffuser is charged with beet cuttings it is closed and warm water is forced into it. The water takes up a portion of the sugar, and then enters a second diffuser, charged with fresh cuttings, or 'cossettes,' to use the French name. This operation is repeated until the juice from the first diffuser, having passed through a certain number of cells, leaves the last charged with sugar. After the working of the process has once been established, each cell containing fresh cossettes is first acted upon by the already partly-charged solution from the cell filled immediately before it.

The fresh warm water enters the cell containing nearly exhausted cossettes, and travels through each cell in succession until the juice finally passes out through the cell last filled.

Between each two cells is a vertical cast-iron cylinder, termed a 'caloriser,' which serves to reheat the juice so as to maintain its temperature, or even, if desired, to increase the same. In working a diffusion battery one diffuser is being charged and a second emptied, while the rest of the battery is under pressure.

The arrangement of a battery, whether in a line, or double line, or circle, depends upon the space at the disposal of the sugar manufacturer. The circular arrangement requires a higher building, owing to the position of the slicing machines, but nevertheless it is usually considered preferable to a line battery. Among the special advantages of a circular battery is the economy of labour. Another important advantage is that all the diffusers are under the immediate control of the workman in charge. The beet slicer is placed above the battery, a swinging shoot conducting the cossettes into the diffusers. The exhausted cossettes are dropped into a channel below, and thence carried to continuous presses by a chain and bucket elevator. As already indicated, the line battery differs from the circular only in the arrangement of the diffusers and the carrier necessary to charge them. A continuous diffuser has been invented by M. Charles, and afterwards advantageously modified by M. Peret, of Roye, France. It is thus described in the 'Bulletin de la Société Industrielle d'Amiens,' 1882. The continuous diffuser consists of an iron cell, cylindrical in form, resting horizontally upon a foundation of masonry. Within this cell is a perforated iron cylinder about 4 feet in diameter and 36 feet in length. The axis is formed by a smaller cylinder. Between these two cylinders is a helix. The inner cylinder is made to rotate, and the speed is so adjusted that it requires sixty minutes for the beet cuttings to traverse the length of the helix. The cossettes are continually immersed in the solution. The water enters the cell at the end, where the exhausted cossettes are expelled. An automatic arrangement controls the amount of water admitted and keeps it at a certain level. The water gradually becomes charged with sugar, and finally leaves the cell at the end where the fresh cossettes enter it. The conditions for a good diffusion are thus carried out, the cossettes and water moving in opposite directions, and the juice becoming more and more concentrated as it comes in contact with cossettes richer and richer in sugar. The water enters at a temperature of 30°C., and is heated as it passes by means of coils placed between the fixed cell and the revolving cylinder, its temperature being gradually increased to 75° or 80°C., and then, as it strikes fresh cossettes, it becomes colder, and leaves the diffuser at a temperature of 50° to 60°C. Three small vertical test cylinders are placed at equal distances from one another, and serve for determining the sp.gr. and the temperature of the juice.

In Germany and Austro-Hungary 90 p.c. of the sugar manufacturers employ the diffusion process. The proportion in France is much smaller, owing to the duty having, till lately, been based upon the sugar actually obtained, and not on an estimated yield. Since the passage of the new law levying the duty on the weight of the roots of an assumed richness, as in Germany, many French sugar manufacturers have adopted this process. It is likely that in a few years the diffusion process will be the only one employed for extraction, except in a few districts where local conditions prevent its adoption.

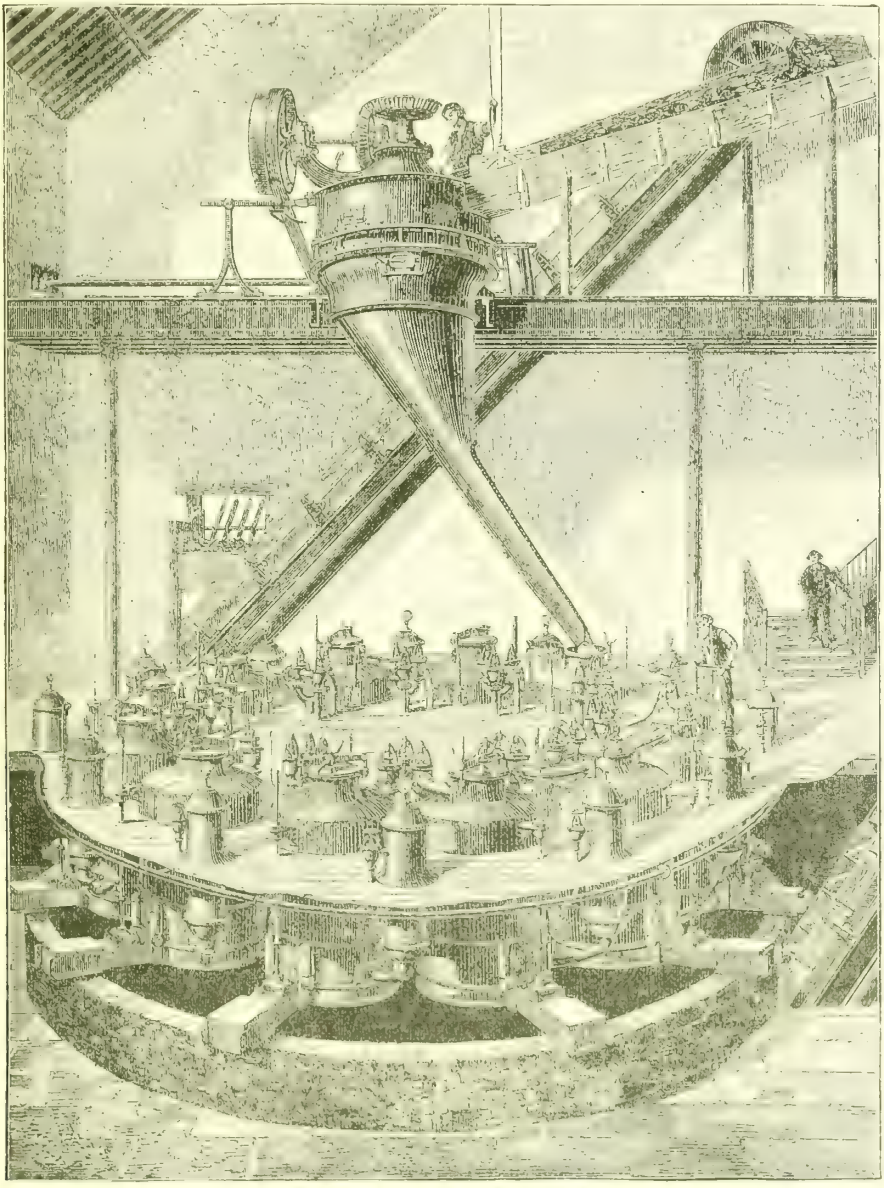


Fig. 7.—Battery of Diffusers.

The beetroot pulp, after the juice has been squeezed out or separated by the diffusion process, serves as cattle food. The transport of beetroots from the field to the factory is frequently attended with considerable expense. To lessen this, the system introduced by Linard, of Cambray, of sending the juice to a central factory by means of underground piping, is sometimes adopted. The juice is treated with 1 p.c. of lime, and then pumped through cast-iron pipes, which are from $2\frac{1}{2}$ to 5 inches in diameter and are capable of withstanding considerable pressure. This system is used to a small extent both in France and Belgium.

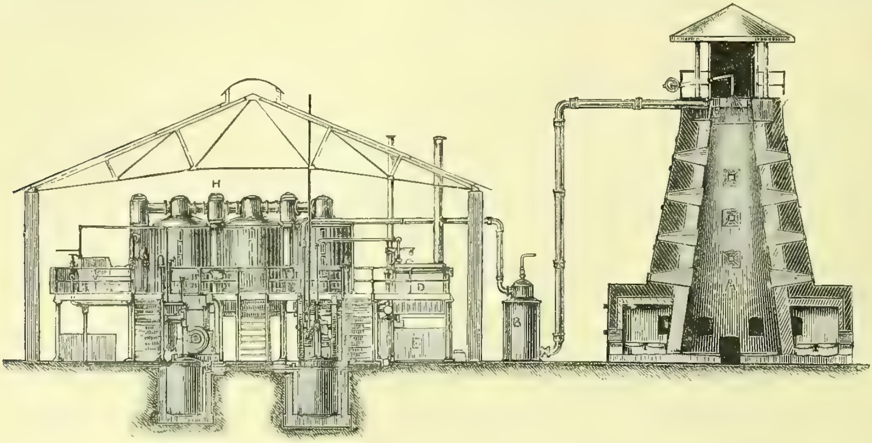


Fig. 8.—Carbonatation Plant (Elevation).

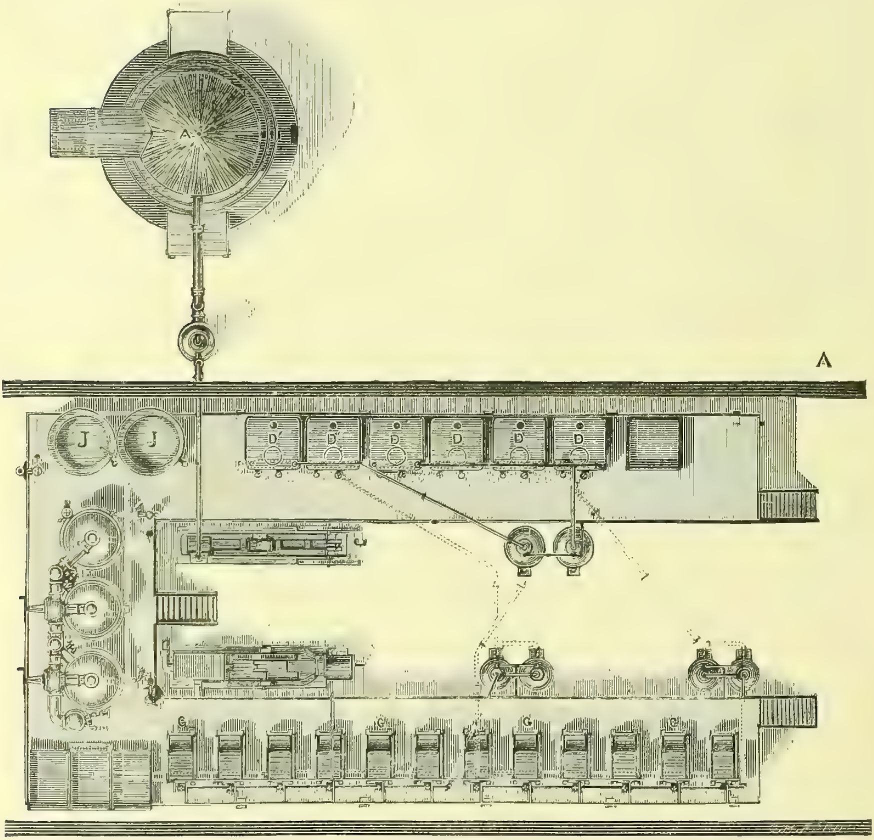


Fig. 9.—Carbonatation Plant (Plan).

As an example, the central factory of Coulommiers (Seine and Marne), belonging to the Fives-Lille Co., may be mentioned. This factory is fed by the four rasping machines of Coulommiers, Jouy-le-Chatel, Vaudoy, and Rozoy-en-Brie by means of underground pipes, having a total length of about twenty miles. This central factory operates each season upon the juice from 45,000 to 50,000 tons of beetroot, and produces 2 500 to 3,000 tons of sugar.

The beet juice resulting from either rasping or diffusion is defecated in a tank fitted with a steam worm, where it is heated to about 85°C. being at the same time mixed with an amount of lime which may range from 0·5 to 3 p.c. on the roots treated, and it is thereby rendered strongly alkaline. The application of heat is continued until the liquid is on the point of ebullition, and begins to break through the scum. The clear juice is then decanted into another tank placed on a lower level, and, whilst still hot, carbonic acid gas is pumped into it through a perforated worm till the alkaline reaction has almost entirely disappeared, or, in other words, till the lime has been precipitated, carrying down with it various impurities. The juice is allowed to stand until it becomes bright, when it is decanted. This process is known as 'carbonatation.' Many impurities, including some of the colouring matters, are removed from the juice by the defecation and subsequent carbonatation, which are usually repeated. In the second carbonatation, however, the amount of lime employed is very much less than in the first. At present the defecation and carbonatation are, in many beet sugar factories, combined in one operation. The carbonic acid gas is obtained from a specially-constructed lime-kiln, and is washed prior to being pumped into the carbonatation tanks. The scum and deposited matter are separated from the remaining juice by means of a filter press. The accompanying engraving (fig. 10) depicts one of the filter-presses commonly used.

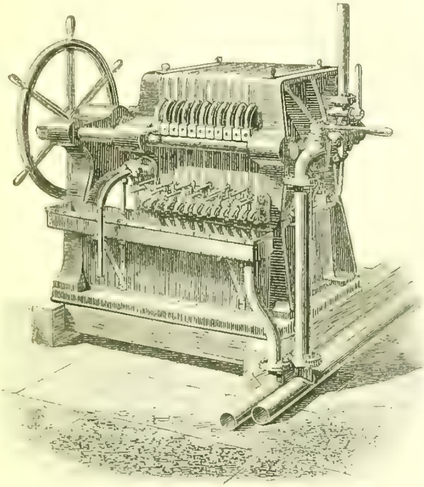


FIG. 10. –FILTER PRESS.

The clear juice is then passed through animal charcoal. In some factories treatment with sulphurous acid and subsequent filtration through sand is made to take the place of animal charcoal. The juice is afterwards concentrated by evaporation to about 20°Bé. in vacuum pans. These are generally arranged in sets of three or four, forming what is known as the 'triple-' or 'quadruple'-effects.

The vapour from the juice in the first pan is used to heat the second, in which the vacuum is more perfect; the vapour from the juice in the second pan is employed to heat the third pan, in which the exhaustion is most complete. Sometimes a fourth pan is added to the set.

This forms the well-known system of evaporation which utilises the latent heat of the vapour of liquids boiling under a low vacuum to boil a second pan under a higher vacuum. The usual limit to this system is four pans, thus utilising the latent heat four times, and reducing the fuel to nearly one-fourth of that required for open evaporation, or single vacuum pans. As generally arranged, all the boiling liquids in the system are under a partial vacuum. Thus in a quadruple effect the first is under a very slight vacuum, from which the vapour is taken to boil a second under 12 inches vacuum; from this to a third, boiling under 19 inches vacuum; and from this to a fourth, boiling at the highest vacuum practically obtainable.

In the engraving of the carbonatation-apparatus and triple effect, vessels are shown under the name of 'syrup eliminators.' These are sometimes used in connection with the second clarification, for bringing the syrup to a sharp boil so as to coagulate albuminous matters &c., the temperature in the triple-effect apparatus being too low to accomplish this unaided. This bringing of syrup to a high temperature appears to be very important where bright sugars are required. For a long time sugars made by the triple-effect process were not so bright as those made with preliminary evaporation in the open air, but giving the syrup a thorough boil between the triple effect and the vacuum pan appears to remedy this defect. The circular gutter round the top of the eliminator permits the scum to be easily brushed off the surface of the boiling syrup.

Another mode of evaporation, which is also worked on the principle of a multiple effect, is called, after its inventor, the Yaryan system, and is somewhat largely used in the United States and elsewhere for concentrating sugar solutions. It differs from various other systems by performing the evaporation within pipes laid horizontally and surrounded by steam. The feed and discharge of liquor to and from the pipes is continuous, and the quantity of liquid within the pipes at any given moment is but small. The liquid thus merely forms a film, which is moved on by the current of vapour, and passes backwards and forwards five times the length of the apparatus, being then discharged into a receiving-chamber, from whence it is pumped into the next effect. The time required for evaporating juice from 6°Bé. to 30°Bé. by this process is said to be only five minutes. The evaporation is conducted in vacuo, and is worked in several separate effects, the steam from the first effect being used to heat the second, and so on as in the ordinary triple effect. For engraving of the Yaryan and other forms of multiple effects *v.* article on EVAPORATION.

Another vacuum apparatus of a somewhat similar kind is known as the 'Lillie Evaporator.' In this apparatus the tubes, which are externally heated by steam, are arranged vertically, and the liquid is made to flow down in a thin film so as to cover the entire interior surface of the tubes.

Apparatus constructed on the system of the Yaryan and Lillie evaporators are known as 'transit evaporators.'

After the beet juice has been concentrated as above-mentioned to 20°Bé., it is again passed through animal charcoal, and, lastly, concentrated in an ordinary vacuum pan until it forms 'massecuite.' The massecuite is then machined in a centrifugal machine, and yields the first crop of sugar, or the first jet. The syrup from the first jet is again boiled down and gives massecuite, which, on machining, yields the second jet sugar. The syrup from this is again concentrated to massecuite, which is allowed to remain for a considerable time in tanks kept in a warm place, when it gives, on machining, the third jet sugar. By again operating in a similar way, a fourth jet sugar is sometimes obtained. Each of the latter jets or crops of sugar is decidedly inferior to the preceding. Even the first jet is, on account of its disagreeable taste and odour, utterly unfit for direct consumption. By washing it, however, with water or steam in a centrifugal machine, the sugar is rendered nearly pure, and is known in the market as 'beet-crystals.'

Yield of sugar. Beetroot containing 10 p.c. of sugar will yield on an average:—

	Per cent.
First jet sugar	5·0
Second jet sugar	1·5
Third jet sugar	0·5
Sugar remaining in molasses	1·5
Loss in the pulp, scum, filter, &c.	1·5
	10·0

Beetroots are now grown in Germany containing 15 to 18 p.c. of sugar, and with such roots the yield of the first and second products will be considerably higher than that above given.

The final molasses are treated by various processes for the partial recovery of the sugar, or they are fermented and distilled, the residue, which contains a considerable amount of potash salts, being used as a manure.

Beet molasses may be represented as having the following average composition:—

	Per cent.
Sugar	50
Other organic matters	20
Ash (mineral matter)	10
Water	20
	100

Among the numerous methods devised for recovering the sugar from molasses, the following are the most important:—

The osmose process of Dubrunfaut. In this process the molasses are placed in an apparatus the sides of which are made of parchment paper, and the outside of which is in contact with warm water. Under these circumstances the salts, which are more easily diffusible than the sugar, pass through the parchment paper, carrying with them, however, a notable proportion of sugar. The sugar remaining inside is comparatively free from saline matters, though it is diluted by the entry of the water to some extent; and in boiling down a considerable amount of sugar may be obtained. This process is used to some extent, particularly in France and Belgium, and is interesting as not requiring, in its execution, the addition of any substance but water.

Lime, baryta, and strontia processes. These depend upon the formation of compounds of sugar with the alkaline earths of an almost insoluble character. These compounds are made by the addition of one of these bases to molasses or other saccharine solutions; the slightly soluble precipitate produced is next washed with water or alcohol, and then decomposed by carbonic acid. The base is thus converted into an insoluble carbonate, from which it can be again recovered, and the sugar is rendered available. Sometimes sucrate of lime is added, instead of slaked lime, to the raw beet juice to neutralise it, the sugar being at the same time set free.

The elution process. In carrying out this process the sugar in the molasses is converted into tribasic sucrate of lime by mixing the molasses with 25 p.c. of lime, when a solid mass is produced. This was washed with water, according to the plan of Lair and Bilange; but as some of the sucrate was dissolved by the water, the use of alcohol was substituted by Dr. Scheibler. A modification of the elution process has been introduced by Seyferth by using molasses at 43° to 44°Be. at a temperature of 30° to 33°C. To this is added 30 to 40 p.c. of finely-powdered quicklime, which is first made into a cream with water. As the lime becomes hydrated, the heat produced causes the mass to dry up. The mass is then broken up in small pieces and placed in vessels called 'elutors,' in which it is systematically washed with alcohol of 35 p.c. After being thus washed five or six times, the sucrate becomes nearly free from impurities, when steam is introduced into the elutor, the alcohol contained in the sucrate distilling off, and the sucrate being reduced to a pasty mass, which can be easily removed. This sucrate may be used to replace the lime in defecating beet-juice.

Manoury's process. This process is similar in principle to the foregoing. Milk of lime is mixed with the molasses in a specially-constructed mixer, and the sucrate of lime leaves it in small grains, which are subsequently washed in close vessels with 40 p.c. alcohol.

Steffen process. In carrying out this process a tribasic sucrate of lime is produced, which is difficultly soluble in water, requiring 200 parts to dissolve it. The mode of operating is as follows: water is added to beet molasses till the density of the solution is 6·6°Bé., the p.c. of the sugar being from 7 to 8. Small portions of lime, which must be freshly burnt and in a finely-powdered state, are then added at short intervals. The temperature is not allowed to exceed 59°F. The amount of lime required to precipitate the sugar is 93·4 lbs. of lime for 100 lbs. of sugar. The sucrate, which resembles a dirty milk of lime, is pumped to the filter-press, which is so constructed that the sucrate can be washed in the press. The mother-liquor is used as manure, and the sucrate is washed with water, the washings being subsequently used to dilute a fresh portion of molasses. The residue in the filter-press, which is nearly pure tribasic sucrate of lime, may be decomposed by hot water, by which two-thirds of the lime is removed and remains in the filter-press. The residual lime is precipitated by carbonic acid, and the sugar obtained by filtering from the carbonate of lime and evaporating the filtrate. The tribasic sucrate of lime is, however, mostly used in the beet sugar fabrics to replace the lime ordinarily employed for defecation. Having seen this interesting process at work, the writers are of opinion that it is the most successful attempt to deal with beet molasses, but at the same time that it is not suitable for the syrups from a refinery in which cane sugar is employed, containing, as they do, a considerable percentage of glucose.

Strontia processes.

The following processes have been patented by Dr. C. Scheibler for the separation of sugar from molasses:

1. Formation of strontium saccharate from the syrup.
2. Separation of the saccharate from foreign substances.
3. Decomposition, by cooling, of the saccharate into strontia crystals and sugar solution containing strontia.
4. Separation of the strontia crystals from the sugar solution.
5. Precipitation by carbonic acid and filtration of strontium carbonate from the sugar solution.
6. Finishing the sugar liquor filtered in the last operation.
7. Recovery of strontia (combined with foreign substances, in the syrup) by means of carbonic acid.
8. Calcination of strontium carbonate to SrO and solution of this oxide to form

$$Sr(OH)_2 + 8H_2O.$$

Dr. Scheibler thus describes the nature of his present modification of the strontia process:—

If to a 20 or 25 p.c. solution of sugar there be added, at 70° to 75°C., with agitation, an equivalent quantity of strontium hydrate, $H_2SrO_2.8H_2O$, a supersaturated solution of strontium monosaccharate is obtained, from which, after a time, either unaltered strontium hydrate may be caused to crystallise out, or the monosaccharate to separate, accordingly as either a crystal of the former or of the latter is thrown in. The monosaccharate referred to has the formula $C_{12}H_{22}O_{11}SrO$ when anhydrous, and the same *plus* $5H_2O$ when crystallised. It is soluble in cold, and more easily in warm, water, and is decomposed, with the formation of the bisaccharate, when a solution is heated above 60°C. One litre of water at 0°C. dissolves 28·4 grms. $C_{12}H_{22}O_{11}SrO$, which is equivalent to 21·8 grms. of sugar. At 58°C. the solubility is 185·1 grms. of the monosaccharate, equivalent to 142·1 grms. sugar. In practice, a strong solution of strontium hydrate, in quantity rather beyond the theoretical, is added to the syrup, the temperature being kept at such a point that no formation of bisaccharate can take place. The mixture, which should remain clear, is then cooled, and a little crystallised monosaccharate thrown in, when the separation of the same compound begins, and is completed after from 12 to 24 hours. The mother-liquor is then pressed out, supersaturated with strontium hydrate, and the whole boiled. A formation of bisaccharate at once takes place; this is removed, and mixed with a fresh quantity of syrup in the proportion of 1 molecule of total sugar to 1·25 molecules of strontium oxide. The mixture is cooled, and a second small crop of monosaccharate obtained as before. From the monosaccharate procured in these two operations the sugar may be obtained after precipitating the strontia as carbonate; or, better, if a crystal of strontium hydrate is thrown into a saturated solution of the monosaccharate, the whole being well cooled; a portion of the strontia then separates as SrH_2O_2, and the remainder is precipitated by carbonic acid. It is claimed that by this process, as compared with the earlier bisaccharate method of the same inventor, a considerable economy of strontium hydrate is effected, whilst the product is purer.

Sucrate of lime process. This process was invented by Boivin and Loiseau. It consists of the purification of sugar solutions by means of a so-called compound termed the 'sucrate of hydrocarbonate of lime,' which is obtained by passing carbonic acid gas into a solution containing sucrate of lime, so as to partly, but not entirely, decompose the sucrate. This sucrate is sometimes used directly in the treatment of cane juice. It is also applied in refining sugars of a high standard not containing more than 2 or 3 p.c. of glucose. In this case the sucrate is mixed with a solution of the raw sugar, and the mixture is then boiled and filtered. Carbonic acid gas is then passed through the filtered liquor to remove the lime as carbonate. The glucose is destroyed by this process without darkening the liquor, as is the case when lime is warmed with liquors containing glucose. The advantages said to result from this process are: decreased cost of working, great saving of animal charcoal, and increased yield of sugar. The molasses left after this mode of working are only fit for converting into spirit. A sample gave, on analysis, the following results:

	Per cent.
Sugar	44·00
Glucose	1·47
Ash [1]	12·96
Water, &c.	41·57
	100·00

The alum process of Duncan and Newlands. The greater part of the saline matter in beet molasses consists of potash salts, and the main object of this process is to remove the potash. This is effected by adding to the molasses in the cold a strong solution of sulphate of alumina, in quantity sufficient to form potash alum with the whole of the potash present. The mixture is well stirred, and in a short time the alum settles out and may be removed, either by decantation or by means of a filter-press. The acid liquor is immediately neutralised by adding milk of lime. The whole is then heated to 160°F., and passed through Taylor-filters or a filter-press, as in the ordinary process of refining. The advantages of this process are: (1) the removal of potash and ammonia from syrups without much dilution; (2)

[1] Containing lime, 2·86; potassa, 1·73.

the removal of much colouring and albuminous matters; (3) considerable improvement in flavour and odour; (4) the alum produced is fully equal in value to the sulphate of alumina used, so that the expense of the process is not great; (5) the plant required is of the simplest description, the cost of labour is small, and the operations are continuous and rapid.

Acetic acid process. It has been proposed to dissolve out all the impurities from molasses by means of concentrated acetic acid, in which sugar is insoluble, but this plan has not been adopted on a large scale.

Margueritte's process. In this process enough sulphuric acid is added to convert all bases present in the molasses into sulphates; a large amount of alcohol is then mixed with the molasses, and a considerable proportion of the bases is precipitated in the form of sulphates. The alcohol is redistilled and used over again, and a good deal of the sugar is recovered. This plan, however, when carried out on the large scale, was not found to give satisfactory results.

Palm sugar. Palm sugar, sometimes termed 'date sugar,' is obtained from the juices of some varieties of palm which are grown in the East Indies, including Hindostan, Ceylon, and the Eastern Archipelago. The juice obtained by making incisions in the tree is boiled down to a solid mass, which is afterwards roughly purified. A good deal of this raw sugar is brought over to Europe and sold as Palmyra Jagghery, a sample of which gave the following results on analysis:

	Per cent.
Sugar	78·00
Glucose	8·93
Ash, soluble	1·71
Ash, insoluble	0·86
Moisture	6·74
Undetermined organic matters	3·76
	100·00

Maple sugar. The sugar-maple (*Acer saccharinum*) is one of the largest trees of the genus, frequently reaching a diameter of 3 to 4 feet, and occasionally attaining a height of over 100 feet. Incisions are made in the trunk a few feet from the ground, and sometimes also in the larger branches, into which wooden or metal tubes are inserted from which are suspended vessels to collect the juice. The sap is heated in a boiler till it thickens, and then is poured into wooden moulds or earthen pots in which it solidifies on cooling. Three men can, according to Michaux, attend to 250 trees, which would yield 1,000 pounds of sugar, or about four pounds per tree. The maple sugar made in the United States and in Canada is entirely employed for local consumption.

A sample of maple sugar (brown sugar) from Canada gave the following analysis:

	Per cent.
Sugar	89·00
Glucose	2·50
Ash	0·54
Moisture	4·30
Undetermined organic matters	3·66
	100·00

Rendement or calculated yield of refined sugar, 83·80.

Sorghum sugar. Sorghum sugar is prepared, to a limited extent in the United States and elsewhere, from the juice contained in the stalks of *Sorghum saccharatum.*

When these are of good quality they contain about 14 p.c. sugar, with about 1·5 p.c. of uncrystallisable sugar. The sugar is obtained in the same way as from the sugar cane.

A great number of experiments have been made in various parts of the United States, under the auspices of the U.S. Department of Agriculture, as to the best means of cultivating the sorghum cane, and also as to the amount of sugar which can be practically extracted therefrom. This investigation has been mostly conducted under the superintendence of Prof. H. W. Wiley, who, in 1888, reported as follows:—The sorghum plant is adapted to large areas of the country which are not adapted to the production of sugar from the sugar cane or from the sugar beet. It is especially adapted to the dry climate of the great West. Its cultivation is suited to the habits of the farming population. When the sorghum plant has been successfully developed, and improved as other sugar-producing plants have been improved, the sorghum-sugar industry will prosper, and will employ capital and labour in producing the sugar which we now import. The sorghum plant is sometimes a good sugar-producing plant, sometimes it is merely a syrup-producing plant. This variability in the chemical composition of its juices is what might be expected from a plant which has not yet been bred up to fixed types of excellence by long-continued selections of seed from the finest plants of the best varieties. Judging by all analogies, the sorghum plant can be very greatly improved by intelligent and long-continued selection.

Preliminary treatment of raw sugar, occasionally made use of before the commencement of ordinary refining.

The raw sugar is sometimes washed by water, steam, or syrup, and is thus separated into two parts, viz. the undissolved sugar, which is purified to a considerable extent by this process, and the washings, which consist of thin syrups, from which, by boiling down, a crop of low-quality sugar can be obtained. One of the most successful inventions for accomplishing this purpose is the 'Weinrich process,' by which the impurities adhering to the crystals of raw sugar are removed by means of steam in a centrifugal machine of peculiar construction, as shown in fig. 11. In working this machine, the ring at the top of the basket is removed and the drum A inserted, care being taken to keep it in the middle of the basket.

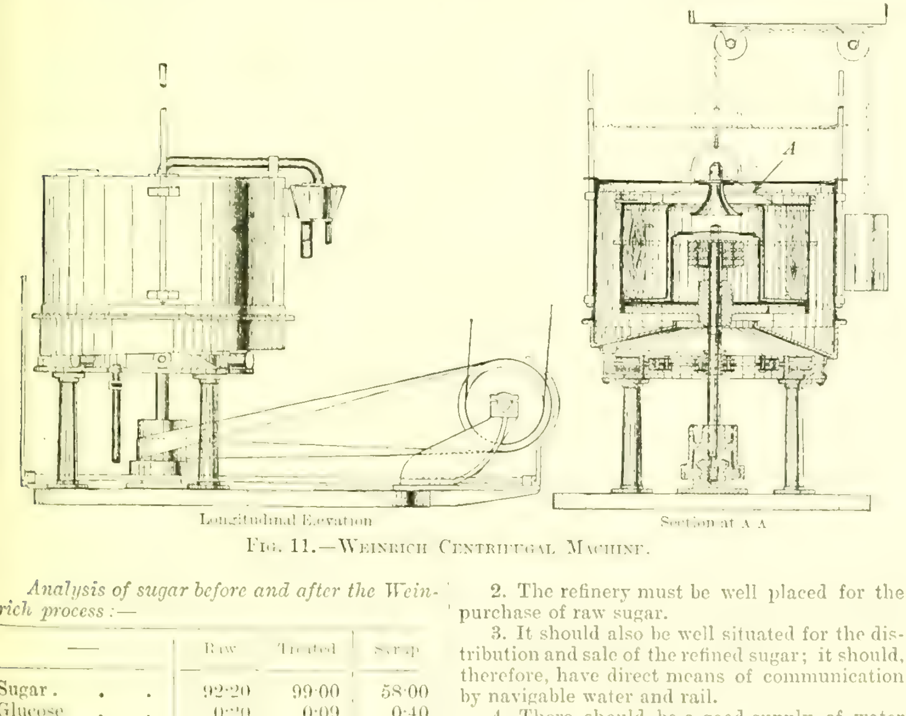
The raw sugar, which must be grainy, is then filled into the space between the drum and the basket, and slightly pressed with the hand. The ring is replaced, the bolts being driven into the bolt-holes with a wooden mallet, and the machine is slowly started. When the sugar is seen to leave the drum, the latter is removed, in a vertical position, by two workmen holding the extremities of the handle.

After the drum is removed, the lid is shut down, the speed of the machine is increased to from 800 to 900 revolutions per minute, and steam is admitted into the interior of the basket.

When the syrup leaving the machine becomes light coloured, the steam is shut off and the machine is stopped as quickly as possible. The lid is then opened and the ring removed, the bolts being driven back with a mallet, and the purified sugar is taken out. If hard sugar be required, wooden wedges are placed in the basket at equal distances apart, the sugar is then introduced, and the operation carried on as before, except that, after the steam has been turned off, the basket is allowed to revolve for two or three minutes before the sugar is taken out, so as to dry the sugar. The wooden wedges are removed by means of an iron rod inserted in the ring at the back of the wedges, and the purified sugar comes out in the form of blocks, which may be roughly broken up or ground in a mill.

When this process is employed, using large-grained raw sugar, the yield of purified sugar is from 80 to 90 p.c., but with low sugars it is from 65 to 70 p.c., the balance of the sugar remaining in the syrup. The treated sugar, if made from good grainy sugar, will polarise from 99 to 99·75 p.c., and if from low sugar 97·5 to 98·5 p.c.

The time required for the operation varies from 10 to 40 minutes, according to the quality of the raw sugar treated. With regard to steaming, the exhaust steam from the engine driving the machines will be more than sufficient. The pressure should not exceed five pounds in the pipes leading to the machines, and the steam should be kept as dry as possible.



Longitudinal Elevation

Section at A A

FIG. 11.—WEINRICH CENTRIFUGAL MACHINE.

Analysis of sugar before and after the Weinrich process:—

—	Raw	Treated	Syrup
Sugar . . .	92·20	99·00	58·00
Glucose . .	0·20	0·09	0·40
Ash . . .	2·37	0·34	3·29
Moisture . .	2·92	0·18	38·31
Other constituents	2·31	0·39	
	100·00	100·00	100·00
Rendement .	80·2	98·3	41·2

Among the more recent improvements in this mode of treatment are the inventions of Walker and Patterson, Frémaux, and Duncan and Newlands.

Sugar refining.

The following are the principal points to be considered in selecting the site of a refinery:—

1. The foundation must be of an excellent character.

2. The refinery must be well placed for the purchase of raw sugar.

3. It should also be well situated for the distribution and sale of the refined sugar; it should, therefore, have direct means of communication by navigable water and rail.

4. There should be a good supply of water for condensing and melting, soft water being preferable for the latter, and for washing the char. If the only available supply should be hard water, it should be softened by Clarke's process or other means.

5. Fuel should be obtainable at a low price.

6. The cost of labour should be moderate.

The process of sugar-refining may be divided into the following operations:—

1. Melting or dissolving in hot water, or weak solutions of sugar, with the aid of open or closed steam.

2. Filtration from mechanical impurities.

3. Decolourisation, by passing through animal charcoal, and also by the action of sulphurous acid.

4. Boiling down or concentrating to massecuite in the vacuum pan.

5. Machining with a centrifugal machine.

These operations will now be described seriatim.

The arrangement of the melting and char departments of a sugar refinery may be understood by reference to fig. 12.

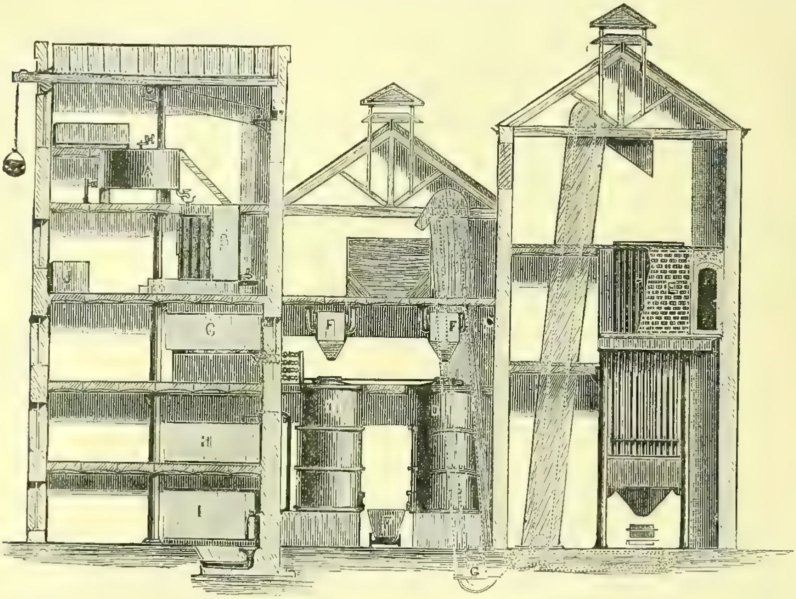


Fig. 12.—Melting and Char Departments of a Sugar Refinery (Elevation)

A. Blow-ups. B. Taylor filters. C. Raw sugar tanks. D. Char cisterns. E. Char kilns. F. Char trucks. G. Char elevators. H. Fine-liquor tanks. I. Sweet-water tanks. J. Washing tanks.

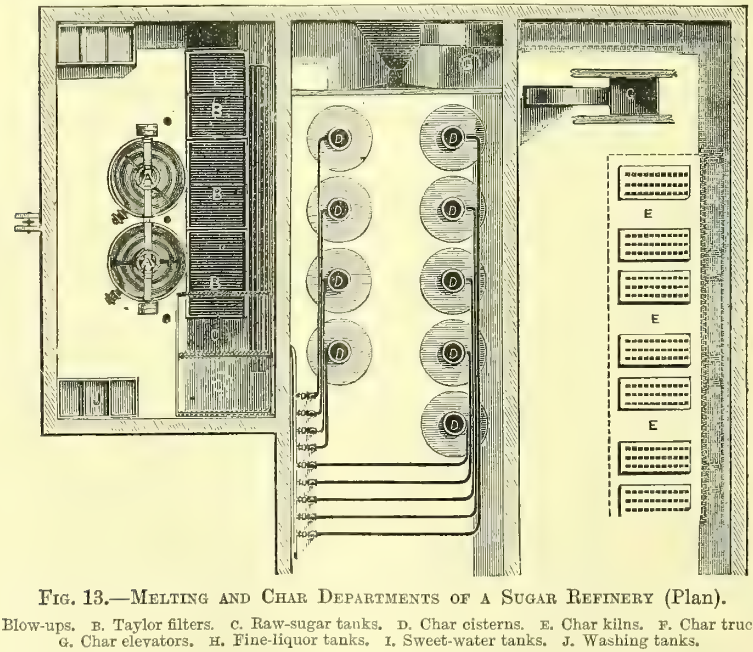


Fig. 13.—Melting and Char Departments of a Sugar Refinery (Plan).

A. Blow-ups. B. Taylor filters. C. Raw-sugar tanks. D. Char cisterns. E. Char kilns. F. Char trucks. G. Char elevators. H. Fine-liquor tanks. I. Sweet-water tanks. J. Washing tanks.

1. *Melting.* The raw sugar is usually hoisted to the topmost floor of the sugar house, known as the 'garret,' and here the various packages are emptied and the contents passed through openings in the floor, preferably covered with iron gratings, the bars of which are at intervals

of about 2 or 3 inches, so as to prevent any very large pieces, either of sugar or other materials, from passing through. Each of these openings is placed immediately over one of the melting-pans, or 'blow-ups,' as they are technically called.

The blow-ups are cylindrical in shape, and are made of cast iron. They are usually placed either in the garret, as shown in fig. 12, or on the floor immediately below it. Each blow-up, A, is capable of holding from 3 to 10 tons of sugar, with water sufficient to dissolve the same; it is provided with stirring gear and a copper coil, which is heated by low-pressure steam, or the coil is perforated with holes so as to blow in open steam. Thus by means of hot water and steam the sugar is rapidly dissolved, and by the addition of more sugar or water, as the case may be, the solution is brought to the required density and temperature, these being about 28°B. and 160°F., or, with low sugars, even a higher temperature. Some cane sugars of low quality, such as jagghery, give a solution which is very difficult to filter, and so blood or some other albuminous substance is added to the solution before the temperature has reached the coagulating-point. On afterwards raising the heat the albumin coagulates and entangles any suspended matters. The cases in which the sugar has been brought, including hogsheads, barrels, boxes, and also mats and bags of various kinds, are thoroughly washed or steamed to get out the sugar.

2. *Filtration.*

Taylor filters. After the liquor leaves the blow-up it is run on to the top of a Taylor filter. The outer part of this consists of a chamber made of cast iron, of various dimensions, provided with doors. At the top of the chamber is a receiving tank from 6 inches to 1 foot deep, covering the entire surface, and in the bottom of this tank are a number of holes about an inch in diameter and about 9 inches apart. Each of these holes is provided with a screw socket to receive the upper end of a bell-shaped brass nozzle which is screwed into it, and round these nozzles the filter-bags are tied. The filter-bags are made of fine twilled cotton cloth, and are about 6 feet long and from 18 inches to a yard wide, and each of them is crumpled longitudinally and slipped inside a sheath made of coarse hempen cloth of an open texture. The sheath is a little longer than the filter-bag, and is from 6 inches to 9 inches in diameter. After the bags are inserted in the sheaths they are tied round the nozzles, which are then screwed into the sockets. Should any one of the bags give turbid liquor the hole at the top of it should be stopped up. After the liquor has ceased to flow freely, the bags are washed repeatedly with hot water (steam being introduced outside the bags to keep the water hot) until all the sweet has been extracted. This bag-water is used for melting raw sugars. The door of the chamber is next opened, and when the filters have cooled down the nozzles are unscrewed, each bag removed from its sheath, and then turned inside out and washed several times in separate tanks. By turning the bag inside out and pushing it under water, the imprisoned air, in escaping, drives before it a good deal of the muddy impurities contained in the bag. This process is repeated several times, each time using cleaner water, and washing the dirtiest bags in the last water. In some refineries the bags are taken direct from the filters in the sweet state, and are washed in the tanks as above described, the mud being afterwards removed from the sweet water by means of a filter press. A little lime is sometimes added to the muddy water to prevent fermentation and assist filtration. For most kinds of raw cane sugar it is necessary to employ Taylor filters, but beet sugar can often be satisfactorily dealt with by means of a filter press. The use of various substances—including lignite, carbonised infusorial earth, brown coal, wood charcoal, animal charcoal, sawdust, &c.—has been suggested to assist the passage of liquor through the filter press, but none of these processes have come into general use, although the last named is employed in a few refineries.

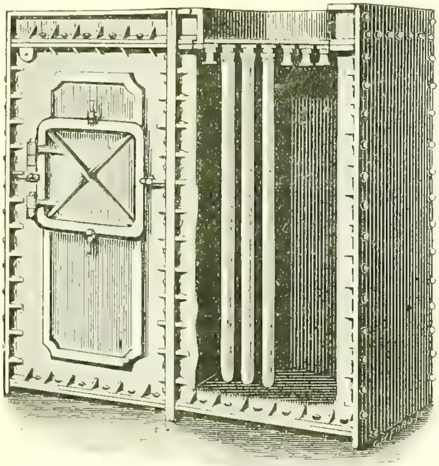


FIG. 14.—TAYLOR FILTER.

3. *Decolourisation.* For this purpose animal charcoal (*v.* BONE BLACK) is employed, being placed in char cisterns consisting of cast- or wrought-iron cylinders, usually about 10 feet diameter by 18 feet high. Each cistern is provided with manholes, one at the top for introducing fresh char and the other at one side near to the bottom for emptying out the char which has been exhausted. Each cistern has also a false bottom made of wood or iron, perforated with numerous holes and covered with scrim cloth, or blankets, so that the clear liquor coming from the char may be deprived of any char dust and may come through perfectly bright. The cisterns are filled with well-burnt char to within a short distance of the top, and the warm liquor is then allowed to flow in at the top, the cock at the bottom of the cistern having been opened to allow the air to escape. When the cistern is full and the liquor begins to come through at the bottom, the cock is turned off, and the whole is generally left at rest for several hours, so as to 'settle.' The cock is then opened, and the decolourised liquor is allowed to flow into

a tank. More raw liquor is at the same time admitted at the top of the char cistern. The speed of flow is so adjusted that the liquor may be sufficiently long in contact with the char to thoroughly utilise its power of removing the colouring and other organic matters from solution. As long as the liquor passing through the char is colourless it is allowed to flow into the same tank and is used for making white sugar. When the liquor begins to assume a yellowish tinge, it is diverted into another tank, and is used for producing a lower grade of sugar. It is usual to proceed in this manner until the liquor passing away from the cistern is of a light-orange colour. The liquor is then turned off at the top, and hot water is run on to drive out the solution of sugar, but as the water mixes to some extent with the liquor a quantity of weak sugar solution is always made. This is known as 'char water,' and is employed in dissolving raw sugar, or it is sometimes, owing to its turbidity and the impurities it contains, treated separately from the liquors. It is a frequent custom to start a char cistern with good liquor, and afterwards to follow this up with lower-quality liquors. The char water, too, is often run into liquor tanks when above 18°B., or as long as it remains bright. When this ceases to be the case, it is run into other tanks until its density is reduced to 1° or 2°Bé., and when this point is reached it is no longer worth saving, and is therefore run down the drain. The washing of the char with boiling water is continued for some hours so as to remove, as far as possible, all organic and other impurities. The char is then allowed to drain, and is removed from the cistern to be dried and reburnt, or, as it is termed, 'revivified,' in the char kilns.

Revivification of char. The kilns employed for this purpose may be divided into two classes, viz. revolving kilns and pipe kilns. The first consist of cast-iron cylinders, revolving in an inclined position and heated externally by fire, through which the char is passed continuously, being turned over in its passage by lifting shelves, and discharging at the lower end into an air-tight chamber. These kilns have of late been almost entirely replaced by the pipe kilns, of which various modifications are employed, the most usual being the one figured in the drawing E, fig. 12. In this apparatus there are two sets of oval-shaped cast-iron pipes, each consisting of three rows placed on either side of a central fire, the heat of which circulates freely among the pipes, raising them to a temperature of about 1200°F. The moist char taken from the char cistern is fed into the pipes, and by the action of the heat is first dried and then carbonised. Below each kiln pipe is a thin sheet-iron cooling pipe, at the bottom of which are two sliding valves, one above the other, and by shutting the top valve and opening the bottom one, a portion of char corresponding to the space between the valves can be discharged. The char falls from the pipes into a storage hopper, from which it is conveyed as required by a travelling band and elevator to a hopper placed above the char cisterns (*v.* fig. 12), and thence by means of trucks travelling on hanging rails, or by conveying bands, to any of the char cisterns which may require filling. For further particulars relating to animal charcoal, *v.* article on BONE BLACK.

4. *Boiling down.* The liquor decolourised, as mentioned above, by passing through char is evaporated down in a vacuum pan, in which, with a good vacuum, it boils at from 120° to 140°F., instead of 220° to 230°F., which it would reach under ordinary atmospheric pressure.

The vacuum pans are made of wrought- or cast-iron, or of copper, the usual shape of those employed in refineries being shown in fig. 15. The lower end is provided with a discharge valve A, and the upper end tapers off into a 'neck' terminating in a safe or 'save-all,' B, connected with an injector-condenser, C, and this is again connected with a vacuum pump D. When it is desirable to economise the water required for condensation, a surface-condenser is employed. If an injector-condenser is used, it is generally provided with a Torricellian vacuum tube to carry away the water, although sometimes the water is pumped out of the condenser by means of the vacuum-pump. The pan is provided with copper steam worms, usually three and a half to four inches in diameter, and also with the following fittings:—

1. Cocks for the admission of steam F, liquor G, and air H.

2. Vacuum gauge I, and thermometer J for indicating the temperature and degree of vacuum.

3. Two or more eye-glasses K, through which the contents of the pan can be observed.

4. A proof-stick L, being a peculiar apparatus by means of which a small portion of the contents of the pan may be withdrawn without admission of air.

The vacuum pan, as shown in the engraving, is steam-jacketed, but they are often made without this addition.

In a refinery, each pan is worked by itself, and they are not associated together in triple, or quadruple, effects. When a partial vacuum has been produced by the aid of the air-pump, enough liquor is admitted by the cock to cover the bottom worm. On turning on the steam, the liquor soon enters into ebullition, and this boiling is kept up until a little of the liquid withdrawn by the 'proof-stick' shows that crystallisation has commenced. Sometimes this crystallisation is induced by the introduction of a small quantity of liquor into the already supersaturated solution. When once crystallisation has commenced, liquor is gradually added, care being taken not to dissolve the crystals already formed, which rapidly increase in size till they form massecuite, which is then discharged from the pan to a receiving vessel usually known as a 'heater,' shown immediately below the vacuum pan in fig. 15. If it be desired to get large grain, when the pan is nearly full a considerable portion of its contents is allowed to run out and the valve is then closed. Fresh liquor is now introduced until the pan is again nearly full, and, the boiling being continued, the sugar from this is deposited upon the surface of the crystals left in the pan. This operation, known as 'cutting,' is repeated several times, yielding each time larger and larger grain. It is generally the practice to raise the temperature of the massecuite 10° to 15°F. before discharging or 'letting-go' to render the mass less viscous. When large crystals are required, crystals are often put in the pan with the first liquor. If the object be to produce soft sugars, or 'pieces,' a larger quantity of liquor or of syrup from a previous operation is introduced into the pan, to commence with, and this being boiled down to the crystallising point, yields a greater number of small crystals, each of which, acting as a centre of crystallisation, lessens the time of boiling, thereby producing a massecuite of smaller grain. The larger crystals are boiled at a comparatively high temperature, from 160° to 190°F., and the pieces at from 120° to 140°F. The time of boiling, in the former case, is from two and a-half to three times as long as in the latter. A pan of crystals will thus take from eight to ten hours to boil, whilst a pan of pieces or loaf-sugar will take from two and a-half to four hours, the time varying with the heating surface of the pan, the density of the liquor, &c.

5. *Machining. Centrifugal machines.* Three of these are shown in the lower part and on the left-hand side of fig. 15. On leaving the vacuum pan. the massecuite passes into the 'heaters.' These are either made cylindrical, or in the shape of a trough, and are generally fitted with stirring gear, being also sometimes heated with steam jackets, whence the term 'heater' was derived. Various means are employed to convey the massecuite from the heater to the centrifugal machines. Metal trucks running on rails are often used, each being large enough to charge one centrifugal machine. The truck is run below the heater, and a valve at the bottom of the latter is then opened until the truck is full of massecuite. The full truck is next run over the top of a centrifugal machine, which has been already set in motion, and is running at a somewhat low speed. A sliding valve at the bottom of the truck is now opened, and its contents fall into the moving machine. The velocity is then increased, and a little water is sometimes added (towards the end of the operation) to assist in washing out the adhering syrup. The speed at which the centrifugal machines are worked depends upon their diameter. The smaller machines, about 3 feet in diameter, are run to 1,000 or 1,200 revolutions per minute, whereas with machines of 6 ft. diameter it is not usual to run at more than 500 revolutions per minute. When the sugar is deemed to be sufficiently dry, the machine is stopped, and the sugar is removed through openings in the bottom of the machine, which have been closed up during the machining, or it is sometimes taken out from the top. In the case of some special centrifugal machines, such as Weston's and Hepworth's, fig. 16, the baskets of the machines are suspended from the side of a horizontal trough-shaped heater, and a valve is provided opposite each machine, so that

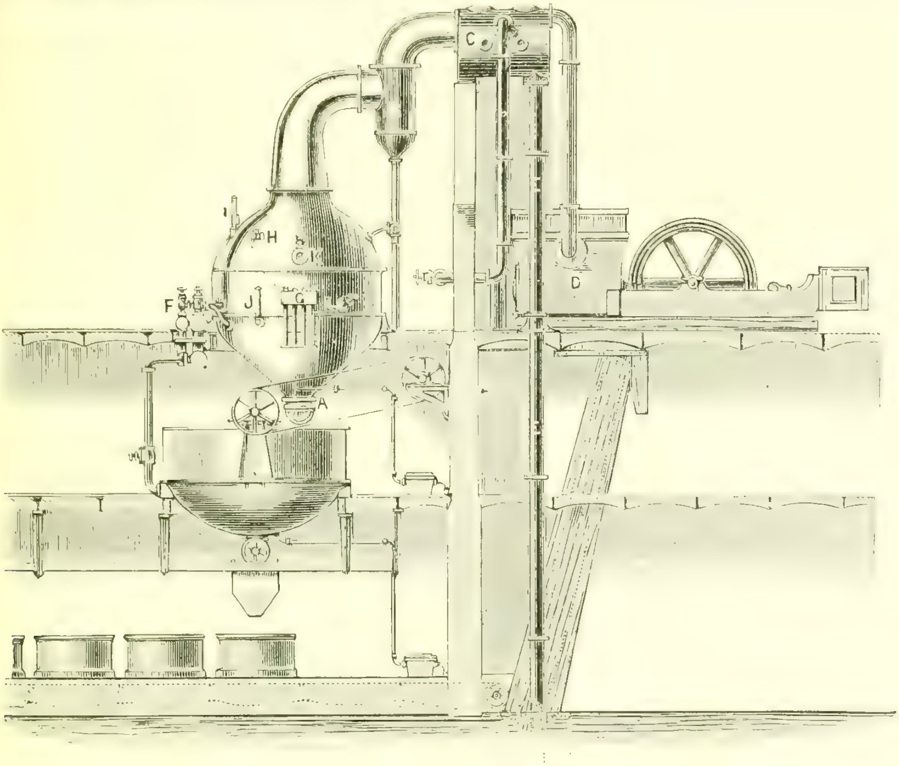


Fig. 15.—Vacuum Pan.

the contents can be delivered direct into the machine.

If the massecuite machined is of low quality, the resulting sugar, on leaving the machine, is allowed to fall upon a riddle which is kept moving backwards and forwards, and any syrup knobs are broken up by hand and mixed with the rest of the sugar.

The sugar is then conveyed, either in small waggons or by means of bands, to the fill-house. Here it is thoroughly mixed, so as to obtain a uniform article, then put into bags holding 2 cwts. each, and weighed.

The syrup from the centrifugal machines is again concentrated and yields another crop of sugar; or it is mixed with the bag-washings and the sweet-water from the char, and used for making a lower quality of raw liquor.

When, by reason of their impurities, syrups cease to yield any crystallisable sugar, they are sold as treacle. Sometimes the lowest syrup is warmed up with dilute sulphuric acid, so as to invert the sugar it contains; it is then neutralised with carbonate of lime and filtered from the sulphate of lime. It is next passed through char, and, lastly, it is boiled down in a vacuum pan, and put into vessels in which it solidifies after standing, forming what is known as 'saccharum,' which is used in the manufacture of beer.

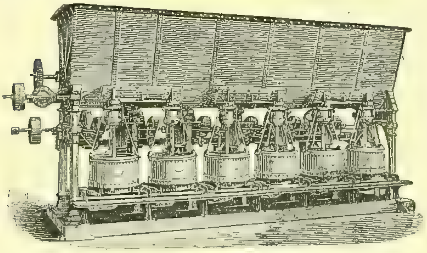


Fig. 16.—Hepworth's Centrifugal Machines.

The 'in and in' system. In many of the Scotch, and also in some English, refineries, no syrup is turned out, but the syrup resulting from the last products of one day is returned to form part of the next day's melting. To work this system with success it is necessary to employ raw sugars of a good description. The products of this mode of working are a first, second, and sometimes a third quality of white sugar in the form of small crystals, and two or three lower kinds of what is known as moist sugar or 'pieces.'

The use of this system favours the production of a large turn-out, owing to the rapidity with which the sugar is refined, the first product being often ready for sale the day after the raw sugar has entered the refinery, and the remaining products within two or three days.

Loaf Sugar. Liquor of good quality is boiled in a vacuum-pan to a fine-grained thick massecuite, which, after being heated in a steam-jacketed heater to about 180°F., is run into conical sheet-iron moulds. The moulds are placed on the floor at the basement of the refinery. They are arranged in rows touching and supporting each other. Before being filled, the small hole at the pointed end, or nose, of each mould is closed by means of a screwed-up rag, or, better, by a wooden spigot. The moulds remain in the fill-house from 10 to 12 hours, during which their contents are stirred up until the mass becomes thick and there is no danger of the crystals settling out and so rendering the loaf of unequal texture. When their contents are set, the moulds are removed to one of the upper floors of the refinery, and the plug closing the hole in the nose of each mould being removed, a pointed iron rod is inserted into the sugar to the depth of 2 or 3 inches to facilitate the drainage of the syrup. The moulds are next placed in holes in racks or stages, and the so-called 'green syrup' drains away into gutters placed beneath. The stages are generally made of wood, and the holes are arranged at such a distance apart that the rims at the top of the moulds may touch and afford mutual support. After remaining on the stages for about 24 hours the green syrup ceases to run, and the soft surface of the sugar is then removed, and mixed with a perfectly colourless and nearly saturated solution of sugar (fine liquor) forming a magma which is then replaced in the mould, thus making a flat, porous surface, through which the fine liquor, afterwards employed for washing the sugar, passes in a slow even stream. By this means the danger of the fine liquor taking a short passage through the loosest part of the loaf is avoided. When the surface of the magma has become dry more fine liquor is run on, and this operation is repeated several times until the syrup running away is colourless. When such is the case, the sugar is allowed to drain until only a few inches of the pointed end or nose remains in a moist state; the syrup from this may be removed by suction or centrifugal force, but the usual practice has been to cut the moist end off. The upper surface of each loaf must also be removed, the sugar obtained in each of these operations being used for making fine liquor. The loaves are now removed from the moulds by inverting the latter and striking them on the rim against a hard block of wood. Each loaf is next placed on its base, in racks, one above the other, heated by steam pipes or hot air to about 120°F. Sometimes the loaves are covered with paper before they are dried in the stove to avoid the danger of cracking through accidental currents of cold air. The time occupied in these various operations depends in a great measure upon the quality of the raw sugar employed, and the grain of the fine sugar produced, but it may generally be said that the process from beginning to end occupies from 10 to 14 days, and that the sugar is for about half this time in the stoves. Owing to the slowness of this process attention has been drawn for some years to the importance of finding some more rapid mode of working, and the result has been that numerous inventions have been brought out and patented for this purpose. These inventions may be divided into two classes. Firstly, those producing moulded sugar from massecuite in the form of slabs or sticks; and secondly, those producing sticks or cubes of sugar, by means of pressure, from soft white sugar which has been dried and purified in a centrifugal machine. Under the first named category, the most important is Langen's process. In this process, the massecuite is run into small segmental moulds divided every $\frac{3}{4}$ in. or so by means of movable iron plates. The moulds are placed one upon another, with a perforated plate, the edges of which are covered with cloth, to make a joint, in between, and they are held down to the top of an iron truck. They are then filled, and allowed to remain till the sugar has set, when the moulds are taken apart and placed in a special centrifugal machine, by which the green syrup is removed. Then they are taken to another centrifugal machine, in which the sugar is washed by fine liquor, this process being repeated, if necessary. These two operations are sometimes effected in the same machine. The sugar slabs are afterwards dried in a stove and cut up into cubes. Duncan and Newlands have also devised a plan of producing moulded sugar, in the form of sticks, which has been somewhat largely used. The principal processes in use for making pressed cubes are those of Hersey and of Pzillas.

The Hersey Patent Cube Machine. By means of this machine (see fig. 17), cubes are made in the following way: Perfectly white moist sugar of good quality as it comes from the centrifugal machine is fed into the hopper at the top of the machine, and is then automatically mixed with a small quantity of liquor, just sufficient to cause the grains to bind together. At the bottom of this hopper is a hollow revolving drum, in the periphery of which are rows of moulds, each of the size of the cube it is intended to make. These moulds are open at the top, but are closed at the bottom by movable plungers connected together by iron bars placed parallel with the axis of the drum. These bars are caused to advance or retreat by means of a cam arrangement. The sugar falls from the hopper into the row of moulds which happens to be under it, and in which the plungers are withdrawn by the action of the cams to their fullest extent; the drum then moves, causing another row of empty moulds to receive their charge. The full moulds pass behind an iron press plate, extending about half way round the drum, which closes up the top openings, and against this plate the sugar is gradually squeezed, by means of the plungers, until the filled moulds reach the bottom of the press plate, when the cubes are pushed out in rows on to small tin plates, which are carried on a band moving in unison with the drum. The plates containing the comparatively soft moist cubes are then placed in a stove heated by steam pipes, and the sugar on drying becomes hard enough to pack into barrels. The greater portion of the hard sugar consumed in the United States is made by this process. One such machine will convert 250 tons of soft sugar into cubes, weekly,

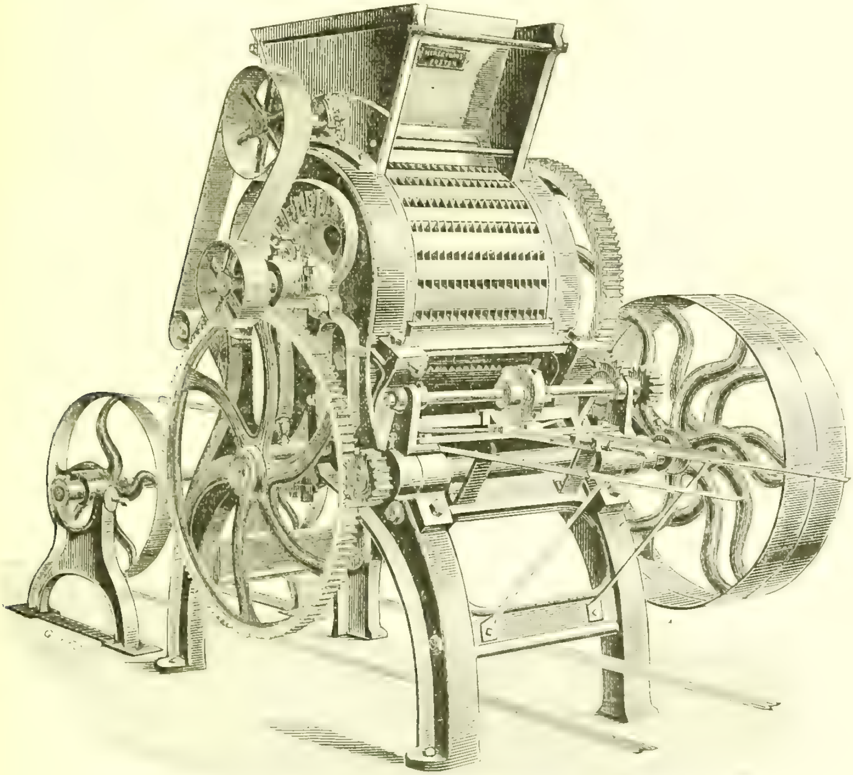


Fig. 17. Hersey Cube Machine.

with a very small amount of manual assistance. The Pzillas Cube Machine, which is largely used on the Continent, was invented prior to the last-described machine, and resembles it in many respects. The sugar, however, is turned out in the form of sticks, and requires to be cut into cubes by means of a cutting-machine. This latter consists of a table on which the sticks, after being arranged side by side, are moved by an endless band, passing on their journey between knives having a reciprocating movement, causing them to cut the sugar into cubes or tablets. Other machines have been devised for pressing sugar, but as they have not come into general use, it is only necessary to say that most of them consist of tables on which are placed metallic plates perforated with square holes which are filled with soft sugar, and are then automatically moved under a plunger, the bottom of which is made with cube-shaped projections which fit into the holes in the plate and press the sugar. The plate is then moved on again over a portion of the table which is perforated in a similar way, and the cubes are pushed through the holes, by means of plungers, on to a travelling band.

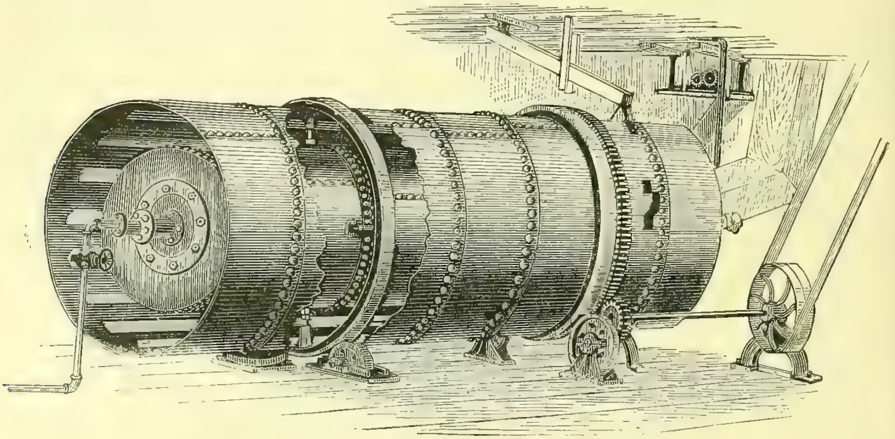


Fig. 18.—Hersey Granulator.

Granulated sugar. An important process for drying or granulating sugar, known as the ‘Hersey Process,’ is now in operation in almost every refinery in the United States and Canada, and has also been adopted in many refineries in Europe and elsewhere. The machine employed for this purpose is illustrated in fig. 18, which shows an elevation in perspective, a longitudinal section through the centre of the machine, and a transverse section on line A B, seen in the longitudinal section.

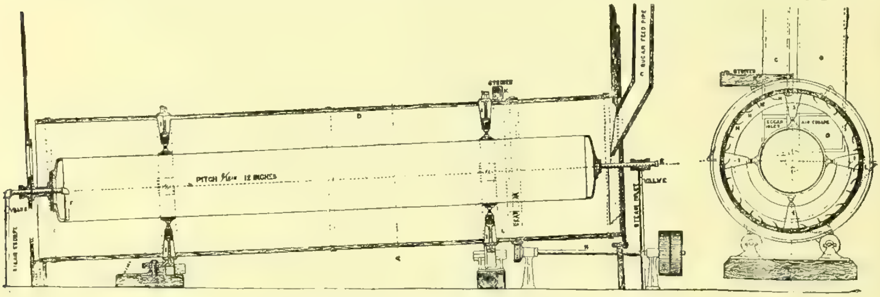


Fig. 19.—Hersey Granulator (Section).

The heating-cylinder C—which is fastened inside of the conveyor-cylinder D, and revolves with it—is filled with steam through the pipe E in one end; and the water of condensation is delivered from the opposite end, through the pipe shown at F, so that the heating-cylinder is always full of steam.

The sugar is fed at one end through a spout G, by a set of rolls placed above the machine, or by a screw-feed; and by the lifting-shelves H H H H, on the inside of the outer cylinder, it is carried up and dropped in a continuous shower upon the heating-cylinder, and rolls off by the rotation of the machine, to be again carried up, working forward to the opposite end by the inclination of the apparatus, and is there delivered into a screen for separating into the different grades. The heater-cylinder is placed centrally within the conveyor-cylinder, and is adjusted and secured by means of the adjusting screws I I I I. The conveyor-cylinder is made of iron; the heater is constructed of steel plate. The conveyor-cylinder is 23 feet long and 6 feet in diameter, with the heater-cylinder 20 feet long and 3 feet in diameter, and makes six revolutions per minute. The striker, K, is for the purpose of removing any sugar that may adhere to the cylinder on first entering the machine, and is worked by the cams L L. The machine is made to rotate by means of the gear M, upon the outside of the conveyor-cylinder, driven by a pinion on the shaft N.

The current of air constantly passing through the machine carries off the moisture from the sugar through the pipe O.

One important feature of the machine is that the sugar being delivered from the end into which the cold air is passing is cool, so that it does not cake, and can be immediately barrelled, and will not cause the barrels to shrink.

The sugar being granulated or dried, not so much from extreme heat but by the moisture being constantly carried from the machine, is brought out clear and white.

Steffen's process. This process has for its object the direct preparation of nearly pure sugar, fit for consumption, from raw sugar without making use of the ordinary refining operations. The method employed by Steffen is very similar to that given long ago by Ritter in his English Patent, No. 9584, 1843.

In carrying out Steffen's process, the raw sugar is first intimately mixed with a quantity of low-grade syrup from a previous operation, which is then replaced by syrups of higher quality in graduated succession, finishing with a solution of pure sugar. The syrups from each washing are collected and kept separate for washing a succeeding batch of sugar of a lower grade of purity, and so on.

The sugar is placed in a battery of cells, or tanks with perforated false bottoms, which are fitted up so that the syrup can be pumped successively from one tank to the next in succession, the contents of which are of a lower quality. By this method of purification there is little or no loss, the yield of sugar nearly corresponding with the amount indicated by analysis.

This process is being extensively used in Germany, and also by Messrs. Say & Co. in France.

Analysis of raw sugars. The four principal substances to be determined are: 1st, sugar; 2nd, glucose; 3rd, ash, or mineral matter; and 4th, water.

The sugar is determined by means of a polariscope, and the most convenient form of instrument to employ is known as the Soleil-Ventzke-Scheibler saccharimeter, made by Schmidt and Haensch, of Berlin.

The process of determining the sugar is carried out as follows: Weigh 26·048 grams of sugar and transfer it by means of a funnel and a little water, preferably hot water, to a 100 c.c. flask. Add sufficient water to dissolve all the sugar, and then cool, if hot water has been used. Add 1 or more c.c. of solution of basic plumbic acetate to precipitate the colouring matters and other impurities. The amount of solution of basic plumbic acetate varies with the quality of the sugar, the darker the sugar the more required, but the right quantity to be added can be easily judged after a little practice. An excess should be avoided, as, on subsequent filtration, the oxide of lead remaining in solution will be precipitated by the carbonic acid in the air, and the solution will be thereby rendered turbid. The addition of a little well-washed aluminic hydrate tends to facilitate the filtration. When cold, the contents of the flask are made up with water to 100 c.c. If there should be any froth on the surface, a drop or two of alcohol should be added just before making up to bulk. The contents of the flask are now to be well shaken, and filtered through a dry filter into a beaker. The first portion passing through must be returned to the filter. Next, take the 200 mm. tube of the polariscope, which must be perfectly clean and dry, remove the screw cap and glass plate from one end, and fill it with the sugar solution. Replace the glass plate and screw cap, taking care not to screw it down too tightly, which might strain the glass plate and affect the subsequent result. On looking through the eye-piece of the polariscope at a lighted lamp, a circular disc will be observed, divided vertically into two equal parts which, when the scale of the instrument stands at zero, have exactly the same tint. On introducing a tube containing a solution of sugar, or any other optically active substance, this equality of tint no longer exists, but by turning a milled head placed below the front part of the instrument it may be again perfectly restored. The percentage of sugar is then read off on the scale by means of the vernier to tenths of a per cent.

Determination of glucose. The glucose is determined by Fehling's solution, which is best prepared as follows: 34·639 grms. of crystallised copper sulphate, which has been powdered and dried by pressing between filter paper, is dissolved in 200 c.c. of water. In a separate vessel dissolve up 173 grms. of pure crystallised Rochelle salt in 480 c.c. of pure solution of sodic hydrate, having a sp.gr. of 1·14. Add the first solution to the second, and make up to 1000 c.c. Preserve the solution in a dark-blue well-stoppered bottle.

In order to standardise this solution, dissolve 2·375 grms. of pure cane sugar in water, and add a few drops of sulphuric acid, then heat to 60°C for a few minutes. Allow to cool, neutralise with sodium carbonate, and make up to 500 c.c. 10 c.c. of this solution contains 0·05 grm. of invert-sugar, and should completely reduce 10 c.c. of the copper test.

The quantity of sugar to be used in the determination of glucose may vary from 1 to 20 grms. in 100 c.c. It is best to make a rough trial with a comparatively strong solution, and afterwards a more careful test with a dilute solution. The best results are obtained when not less than 10 or more than 50 c.c. of the sugar solution are required to decolourise 10 c.c. of the copper test.

The solution of sugar used should be as colourless as possible, and then the exact point is not difficult to hit. 10 c.c. of the copper test are measured into a 4 or 5 oz. flask, and made to boil, and then 3 or 4 c.c. of the sugar solution are run in and the boiling repeated. If any blue colour remains, the sugar solution must be again added, a few c.c. at a time, boiling after each addition, until at last the blue colour entirely disappears. Then read off the number of c.c. used, and refer to a table which gives the percentage of glucose, or calculate it from the weight of sugar taken. Thus, if 50 c.c. of a 1 p.c. solution of sugar were required to decolourise 10 c.c. copper test, it would imply that 0·5 grm. sugar contained ·05 glucose, or there would be 10 p.c. of glucose in the sugar.

If there should be any doubt as to the exact point at which all the copper in the copper-test is precipitated, it may be removed by allowing the red deposit to settle, and then taking a little of the supernatant liquor by means of a small pipette, and testing this for copper by first making it slightly acid with acetic acid, and then adding a few drops of solution of potassium ferrocyanide, by which a brown precipitate of copper ferrocyanide will be produced, or at least a brown colouration if the amount of copper should be very minute. After the copper has been entirely precipitated a small addition of the sugar solution, followed by boiling, will give a yellowish-brown colour, owing to the soda in the copper test acting upon the glucose in the raw sugar. Beetroot sugars contain very little, if any, glucose, and consequently in testing them it is necessary to take a large quantity, say 20 or 25 grms. in 100 c.c., and to use a very small quantity of the copper test.

Determination of ash. From 2 to 5 grms. are weighed in a platinum dish, and then moistened with strong sulphuric acid, the mixture being stirred with a platinum wire. If the sugar be damp to start with, the action of the sulphuric acid is very rapid; if the sugar be quite dry, it should be wetted slightly, or gently heated for a few moments with the sulphuric acid, so as to start the reaction. When this action is over, the dish is heated either over a Bunsen burner or placed in a muffle at a low red heat. As soon as the carbon is thoroughly consumed, the dish is re-weighed. One-tenth of its weight is deducted from the ash to compensate for the increased weight produced by the substitution of sulphuric acid for carbonic acid, &c.

Soluble ash. Should there be any insoluble mineral matter present in the raw sugar, it is necessary to determine the amount of soluble ash, as this alone is instrumental in impeding the crystallisation of the sugar. To do this, dissolve 10 grms. in water and make up to 100 c.c. Well mix and filter through a dry filter. Take 20 c.c. of the filtrate, equal to 2 grms. of the raw sugar, evaporate to a pasty condition; then cool, add sulphuric acid, incinerate, and weigh.

Determination of moisture. Five grms. should be weighed in a porcelain dish and heated to 100°C. till the weight is constant. In working with a very low pasty sugar or with molasses, two or three times its weight of dry sand should be well mixed with the sugar taken, and stirred up at intervals. It is also usual to add a little alcohol to the mixture, and stir it well in with the sand and sugar. The heat applied must be very moderate at first, but when the alcohol has evaporated it may be raised to 220°F., with occasional stirring during a few hours.

Statement of results. This is usually given under the following heads: sugar, glucose, ash, moisture. The difference to make up 100 is put down as undetermined organic matters, &c.

It is generally considered that glucose prevents its own weight of sugar from crystallising, and that the soluble ash prevents five times its own weight of sugar from crystallising, and so, to obtain the yield of sugar—or *rendement*, as the French call it—from a given sample it is necessary to deduct from the percentage of sugar as given by polarisation the amount of glucose and five times the weight of the soluble ash.

Thus a sample of cane jagghery had the following composition:—

Sugar	77·20
Glucose	9·26
Soluble ash	3·43
Insoluble ash (sand, &c.) .	0·24
Moisture	7·36
Undetermined organic matters	2·51
	100·00
Rendement	50·79

The following table gives the production of sugar for the year 1890-1891:—

Beetroot sugar.

	Tons
German Empire . . .	1,331,965
Austria-Hungary . .	778,473
France	694,037
Russia and Poland . .	544,162
Belgium	205,623
Holland and other countries	141,307
	3,695,567

Cane sugar.

Cuba	730,000
Porto Rico	40,000
Trinidad	45,000
Barbados	45,000
Jamaica	25,000
Antigua and St. Kitts . .	30,000
Martinique	32,000
Guadeloupe	50,000
Demerara	116,000
Reunion	39,000
Mauritius	130,000
Java	414,000
British India	60,000
Brazils	175,000
Manila, Cebu and Ilo-ilo .	166,000
Louisiana	220,000
Peru	24,000
Egypt	40,000
Sandwich Islands . . .	115,000
Total of cane . .	2,496,000
„ beet . .	3,695,000
	6,191,000

The following analyses will serve to give an idea of the principal varieties of raw sugar:—

Raw sugars	Sugar	Glucose	Ash	Moisture	Undetermined organic matters
China	79·46	8·62	2·39	4·98	4·55
Dominica . . .	92·80	2·74	1·11	2·38	0·97
Havana . . .	94·00	2·23	0·30	2·06	1·41
Jamaica	91·00	4·17	1·08	3·04	0·71
Manila	82·40	6·94	1·72	4·96	3·98
Peru	94·30	1·99	0·72	2·00	0·99
Porto Rico . . .	91·30	3·60	0·86	3·34	0·90
St. Kitts	89·70	3·91	1·15	4·40	0·84
St. Lucia	89·60	1·48	1·02	2·88	2·02
St. Vincent . . .	90·50	4·00	1·04	3·62	0·84
Surinam	83·00	6·94	1·94	5·56	2·56
Trinidad	88·60	4·31	1·53	3·98	1·58

The writers desire to express their acknowledgments to Messrs. Manlove, Alliott, Fryer & Co., of Nottingham and Rouen, for the drawings which they have kindly furnished for this article. N. Bros.

Saccharimetry. 1. *Polarisation of light.* If an ordinary ray of light emitted from any source whatever be examined, it will be found to exhibit the selfsame properties on all sides—that is to say, it is capable of being reflected or refracted in any position whatever. If, however, this ray of light be subjected to such conditions as will restrict its vibrations to some one particular direction, such a ray is said to be polarised. This may be accomplished by one of the following ways:

1. By reflection.
2. By ordinary refraction.
3. By double refraction.

It is with the last method that this article is most immediately concerned.

2. *Plane polarisation.* It is well known that certain crystals have the property, when a ray of light passes through them, of splitting up that ray into two others of equal intensity. Such a phenomenon is known as double refraction, and such crystals are said to be doubly refracting. In every such crystal there is at least one direction in which no such splitting up of the ray takes place, and this direction is called the optic axis of the crystal. Iceland spar exhibits this phenomenon in a notable manner. In a crystal of Iceland spar the line joining the points where the three obtuse angles meet is the principal or optic axis, and any ray of light transmitted through the crystal in a direction parallel to this axis is not divided. If, however, the crystal be tilted out of this position, the emergent ray is found to be separated into two. The angular divergence of the two rays depends upon the angle through which the crystal has been turned. When this angle amounts to a right angle the separation is at its greatest; and if the crystal be still further turned, the two rays begin to come together again, until, when it has turned through another right angle, they coincide. On examination it will be found that both of these rays are completely polarised, the plane of polarisation of one being parallel to the principal section of the crystal—that is to say, to a plane passing through the optic axis and the direction in which the ray traverses the crystal—the other in a plane at right angles to that section. The first of these rays follows the ordinary law of refraction, and is called the ordinary ray; but the other ray, which is polarised at right angles to the principal section, follows different laws of refraction, and is termed the extraordinary ray. For polarimetric purposes it is best to give exit to only one of these polarised rays—that, namely, which is parallel with the incident ray—and to throw the other completely out of the field of view. This can be done in various ways, but best by means of what is known as a Nicol's prism. For this purpose a rhombohedron of Iceland spar, double its natural length (fig. 20), of which *a*, *b*, *c*, *d* (fig. 21) represents a section, is taken, and the terminal faces *a b* and *c d*, which naturally make an angle of 71° with the sides *a d* and *b c*, as at *a c*, are cut obliquely, so as to give the new faces an inclination of 68° to these edges. The whole block is then divided into two by a cut in the direction *b d*, and at right angles to the new face *a b'*. The faces of this cut are then carefully polished, and cemented together again in their original position with Canada balsam. Such an arrangement is called a Nicol's prism, as shown in fig. 22.

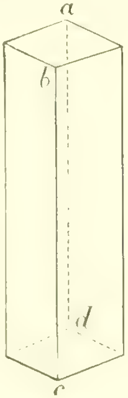


Fig. 20.

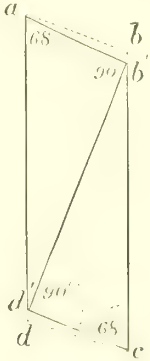


Fig. 21.

If now a ray of light, *l m* (fig. 23), parallel to the edges of the longer side, fall on the face *a b*, it is split up into two rays, both of which are polarised, but at right angles to each other. The less refracted or extraordinary ray *m p q* traverses the film of balsam at p, and emerges in the direction $q\,s$ parallel to $l\,m$. The more refracted or ordinary ray, $m\,o$, meets the balsam at o, which, from its being a medium of so much feebler refractive power, causes *total reflection* of the ray in the direction $o\,r$, whereby it becomes absorbed by the case of the prism. The other ray emerges in the direction of the incident one, but possesses only half its luminous power.

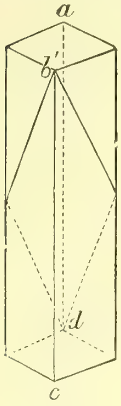


FIG. 22.

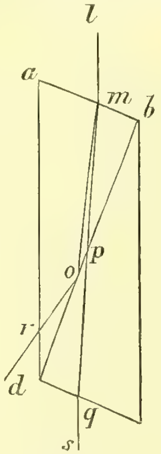


FIG. 23.

The plane of polarisation of this ray (or the plane in which it vibrates) is at right angles to the principal section, and therefore passes through the longer diagonals of the end faces of the prism.

In order to study the behaviour of a polarised ray it is necessary to make use of a second Nicol's prism so placed that its principal axis is in a line with that of the first. Two such prisms, when thus used together, are respectively called the 'polariser' and the 'analyser.'

In figs. 24 and 25 such a combination is shown. In the first case both prisms are arranged so that the plane of polarisation $a'\,a'\,n$ of the analyser A is parallel with the plane of polarisation $a\,a\,m$ of the polariser P, and also the principal section $b\,b\,m$ and $b'\,b'\,n$ of the two prisms are brought into the same direction. The ray m, which enters P as ordinary light and emerges polarised at m', is not decomposed on passing through A; it is merely refracted in the direction of an extraordinary ray $m\,p\,q$ (fig. 23), and emerges so at the opposite end of the analyser.

The same happens if the latter be turned through an angle of 180°, so as to bring the planes again parallel. If, now, the analyser A be turned round so that its plane of polarisation, instead of being parallel, is at right angles to that of the polariser, as is seen in fig. 25, then the ray, after passing through P, when it enters A will take the direction of the ordinary ray, as represented by $m\,o\,r$ (fig. 23), and is eliminated by the film of balsam. No light leaves the analyser, and hence the field of vision appears dark. The same thing happens at a distance of 180°. At all intermediate positions between these two—that is, when the two Nicols are neither parallel nor at right angles to each other—polarised light, as it enters the analyser, is separated into an ordinary and an extraordinary ray, varying in intensity with the angle at which the planes of polarisation of the two prisms are inclined to each other, and the field of vision becomes more or less illuminated.

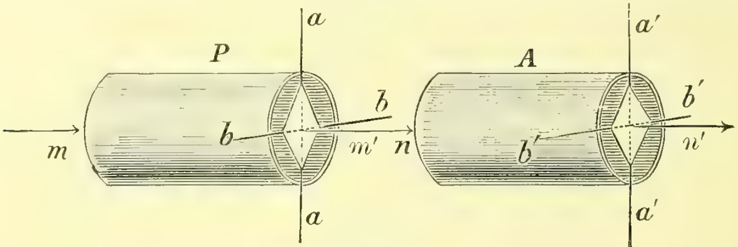


FIG. 24.

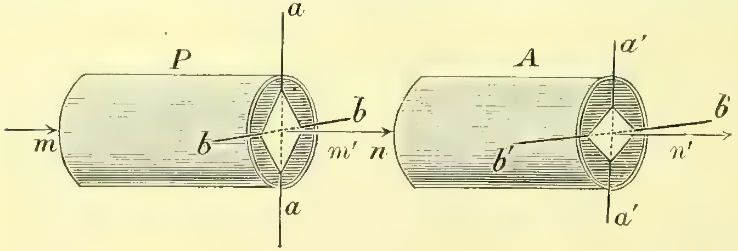


FIG. 25.

3. *Circular polarisation.* When a ray of light passes through a plate of quartz which has been cut at right angles to the axis of the crystal, it is also split into two rays, just as in the case of the Iceland spar; but the

vibrations in each ray, instead of being rectilinear and at right angles to one another, assume a circular course, proceeding in directions opposed to each other; so that if the motion of one ray takes the direction of the hands of a watch, that of the other will be in the opposite direction; and it is evident that the curve traced out by any series of particles at any given time will, under these circumstances, take the form of a corkscrew or a helix, and such may be a right-handed or left-handed helix according to the rotatory movement of the particles to the right or to the left. Now, as may readily be supposed, the velocities of the vibrations in both rays will not be equal, but will be greater or less in one than in the other; hence the difference in velocities will determine the sweep of the helix or the circular direction to left or right of the polarised ray. Such a ray is therefore said to be circularly polarised, and is known as right-handed or left-handed, according to the direction of the motion of its vibrations. Those crystals of quartz which cause the plane of polarisation to rotate to the right or left as the case may be are termed right-handed and left-handed quartz respectively.

If, therefore, whilst the two Nicol prisms are crossed as in fig. 25, so that no light is transmitted by the analyser, a plate of quartz be interposed, a red light makes its appearance on the screen; so that to render the field again dark it is necessary to turn the analyser through a certain angle either to the right or to the left. Whence it follows that the ray which has traversed the quartz must have had its plane of vibration deflected through an angle equal to that through which the analyser has been turned. The angle through which the analyser has to be turned to bring a recurrence of darkness in the field of vision, and which can be read off on the graduated rim of the disc, is called the angle of rotation, and is the measure of the deflection experienced by the plane of polarisation.

Precisely similar effects are produced with yellow, green, violet, or any other kind of homogeneous light; but the angle of rotation varies according to the nature of the ray, being least for red and greatest for violet light, as shown in the following table:

Table I.—*Rotation produced by quartz plates for different rays.*

	Plate, 1 mm.	Plate, 3·75 mm.
Red . . .	19·0	71·2°
Orange . . .	21·5	80·6
Yellow . . .	24·0	90·0°
Green . . .	29·0	108·7°
Blue . . .	31·0	116·2°
Indigo . . .	35·5	133·1°
Violet . . .	42·8	161·0°

If a plate of quartz be used of such a thickness that it rotates any particular tint just 90°, that tint will be cut off by the crossed analyser, and all others will, in greater or less proportion, be transmitted, so that the resulting tint will be complementary to that cut off. For instance, a plate just so thick as to twist the yellow waves round 90° must be 3·75 mm. thick. When such a quartz plate is placed between the crossed Nicols the light shown is yellow; but if placed between parallel Nicols it shows a rich purplish-violet colour, the complementary of the yellow. This particular tint Biot found to be exceedingly sensitive, the smallest inaccuracy in the adjustment of the prisms at once producing a change, the colour appearing either too red or too blue according to the direction in which the analyser has been turned out of exact adjustment. This tint is accordingly known as the transition tint, its accurate definition being due to the fact that the human eye is more sensitive to the presence or absence of the complementary yellow than to any other tint in the whole spectrum.

Biot therefore proposed that, instead of trying to get a restoration of darkness, one should begin with a purple tint and work for the restoration of that tint. And in measuring the rotation produced by various substances, this is often taken as the standard instead of the darkened disc used with monochromatic light. It is therefore evident that the rotative power of substances can be measured in two ways—either by means of monochromatic light, taking as zero a field of either maximum or minimum illumination, or by means of ordinary light with aid of quartz plate interposed, using the transition tint for zero.

This rotation or twisting of the polarised ray is termed circular polarisation, and substances which, like quartz, exhibit this property are said to be circularly polarising, or optically active substances, whilst bodies which do not possess this property are said to be inactive.

Circularly polarising substances may, according to Landolt, be divided into two classes:

I. Bodies which in a crystalline state only possess the property of rotating the plane of polarisation and which lose this property entirely when brought (either by solution or fusion) into an amorphous condition. To this class belong such bodies as cinnabar, quartz, sodium chlorate, sodium bromate, and sodium sulphantimoniate.

II. Bodies which display rotatory power when dissolved in a suitable medium, and are consequently in the amorphous state. Substances of this class are, without exception, carbon compounds, and may be either right (+) rotating or left (−) rotating. To this class of compounds belong most of the carbohydrates and derivatives therefrom, vegetable acids, terpenes, ethereal oils, resins, gums, camphors, alkaloids, albumins, &c.

The fact that substances in class I. exhibit rotatory power only in the crystalline state, and lose it directly they are brought into solution, is proof that the rotation is entirely dependent upon crystalline structure, so that in this state the phenomenon is a purely physical one; whereas in the case of those substances belonging to class II. which exhibit rotatory power in the liquid state, it has been ascertained from determinations, made by Biot in 1817 (Mém. de l'Acad. 2, 114), and later by Gernez in 1864, of the rotatory power of certain of these bodies in the gaseous state, such as camphor and turpentine oil, that the optical activity must be a property resident in each molecule and dependent upon its atomic structure, and hence in this case the phenomenon is essentially a chemical one. As a natural sequence to this a theory was proposed by Le Bel in 1874 (Bl. [2] 22, 337), and by Van't Hoff in 1875 (Bl. [2] 23, 295), which brings into direct connection the rotatory powers and the constitutional formulæ of substances. Le Bel first suggested that when a carbon atom occurs in combination with four different radicles a molecule of asymmetrical shape is constituted, which, as such, should exhibit rotatory properties. Van't Hoff, proceeding on an hypothesis of his own respecting the ultimate arrangement of atoms in space, was led to the same idea.

4. *Rotatory dispersion.* For a complete determination of the rotatory power of a given substance, it is necessary to take the angles of rotation for a number of different rays of known wave-lengths. This can only be fully accomplished with the aid of Fraunhofer's lines—that is, by the use of the solar spectrum.

In the case of quartz the angles of rotation (α) for different lines have been accurately determined by several observers, and are given in Table II., along with the corresponding wave-lengths λ, expressed in millimetres, as given by Landolt in his 'Handbook,' p. 44.

TABLE II.

Ray	λ	α for 1 mm.
B	0·0006871	15·55°
C	6560	17·22°
D	5888	21·67°
E	5269	27·46°
F	4860	32·69°
G	4309	42·37°
H	3967	50·98°

From the foregoing measurements Boltzmann has deduced the dispersion formula:

$$\alpha=\frac{7\cdot07018}{10^6\cdot\lambda^2}+\frac{0\cdot14983}{10^{12}\cdot\lambda^4}$$

For ray D the following values have been obtained by different observers:

Biot, 20·98°; Broch, 21·67°; Stefan, 21·67°; Wild, 21·67°; Von Lang, 21·64°.

The number 21·67 has been generally adopted for quartz. Extending the investigation to other substances, it has been found that not only do the absolute values of rotation in any one substance vary for different rays, but also in different substances the values vary by a different series of proportions—that is to say, different bodies have different powers of rotatory dispersion; thus for ray D:

Quartz	α,	1 mm.	21·67
Cane sugar	$[\alpha]$,	1 dec.	+66·41
Cholalic acid	$[\alpha]$,	1 dec.	+33·9
Cholesterin	$[\alpha]$,	1 dec.	−31·59
Oil of turpentine	α,	1 dec.	−29·3
Oil of lemon	α,	1 dec.	+48·5

And calculating the ratio of rotation experienced by ray D as compared with that by ray B, taking B as unity;

	D
Quartz	1·39
Sugar	1·40
Cholalic acid	1·20
Cholesterin	1·53
Oil of turpentine	1·36
Oil of lemon	1·43

It will be seen from this table that the ratios in the case of sugar and quartz agree very closely; hence it may be taken that these two substances have equal powers of rotatory dispersion, while the others have either more or less than quartz.

Advantage has been taken of this fact in the construction of certain instruments for measuring the rotation of optically active substances, but up to the present this has only been proved to hold good in the case of cane sugar, so that the examination of other carbohydrates, as well as of other optically active substances, cannot be considered as absolutely correct with instruments of this description.

In the majority of instances the determination of the rotation for several rays would be exceedingly troublesome and inconvenient, so that all determinations are now referred to one particular ray. The one uniformly chosen is ray D, which lies on the border between orange and yellow, the light being supplied by a sodium flame.

The wave-length of this ray as given in Table II. is 0·0005888 mm., whilst the amount of rotation produced by a quartz plate 1 mm. in thickness for this ray is 21·67°. The specific rotation of quartz for ray D is designated by the symbol $[\alpha]_D$.

Where white light (argand gas lamp) is used the rotation given is for the so-called transition tint—that is to say, the colour complementary to mean yellow light, the wave-length of which is about 0·00055 mm. The specific rotation obtained for the transition tint is indicated by the symbol $[\alpha]_j$.

Now, the wave-length of this mean yellow light is less than that of the ray D which lies on the border between orange and yellow, and as, according to Biot, the angle of rotation α varies inversely as the square of the wave-length of ray λ, the value of α_j must be always greater than that of α_D. Thus with quartz $\alpha_D=21\cdot67$ and $\alpha_j=24\cdot5$.

5. *Specific rotatory power.* When different active substances, liquids—as for instance, oil of turpentine—are examined in the polarimeter, according as these liquids differ in density varying masses of molecules will be brought to bear upon the transmitted rays; therefore, before any exact comparison can be made, the observed angles of rotation must be calculated to one common density. If the density 1 be taken, as recommended by Biot, the angle of rotation α of the several liquids must be divided by their specific gravity (d). The angle of rotation given by a length (l) of 1 decimetre of any active liquid corrected to the standard density 1 is denominated by Biot the *specific rotation* or *specific rotatory power* $[\alpha]$ of that substance, and may be found from the observed data α, l, and d by the formula

$$\text{I.}\quad [\alpha]=\frac{\alpha}{l.d}.$$

By taking as unit density that of water at 4°C., density becomes synonymous with weight in grms. of 1 c.c. of the substance, and the specific rotation of any active substance may then be defined as the deviation produced by 1 grm. of the substance when occupying a space of 1 c.c. and forming a column 1 decimetre in length for the ray to traverse.

For active solid substances, which when dissolved in distilled water exhibit a rotatory power, he proposed to find a formula as follows:

If P grms. of the substance be dissolved in E grms. of water, and d be the density of the solution, then 1 c.c. (unit volume) will contain $\frac{P}{P+E}.d$ grms. of substance.

If a solution of the above composition in a tube l decimetres long give an angle of rotation α, then the deviation for a solution containing 1 grm. of active substance in 1 c.c. of solution, *i.e.* the specific rotatory power $[\alpha]$, is found by the proportion

$$\frac{P}{P+E}d : \frac{\alpha}{l} = 1 : [\alpha], \text{ whence } [\alpha] = \frac{\alpha(P+E)}{l.P.d}.$$

Let $\frac{P}{P+E}$, that is, the amount of active substance in the unit weight of solution, $=\epsilon$, then $[\alpha] = \frac{\alpha}{l.\epsilon.d}$, and if the proportion of active substance be stated for 100 parts by weight of solution and this proportion $(100\,\epsilon)$ be indicated by p, then

$$\text{II.}\quad [\alpha] = \frac{100\,\alpha.}{l.p.d}.$$

For the calculation of this formula it is necessary to know the percentage, weight, and the density of the solution, but, since $p.d$ equals the concentration c—that is, the number of grms. of active substance in 100 c.c. of the solution—p and d need not be determined separately. The only thing necessary, therefore, is to weigh out the number of grms. of solid substance, dissolve in water in 100 c.c. flask, and dilute the solution to the mark. The equation then becomes

$$\text{III.}\quad [\alpha] = \frac{100\,\alpha}{l.c}.$$

Let the length of the tube in millimetres $=$ L, the above equations then become

$$\text{I.}\quad [\alpha] = \frac{100\alpha}{L.d},$$

$$\text{II.}\quad [\alpha] = \frac{10^4\,\alpha}{L.p.d},$$

and

$$\text{III.}\quad [\alpha] = \frac{10^4\,\alpha}{L.c}.$$

6. *Dependence of specific rotatory power on nature and amount of solvent.* When Biot (Mém. de l'Acad. 2, 41) first determined the specific rotation of cane sugar in 1819, he found that with tubes of equal length the angles of rotation were in direct proportion to the amount of sugar in solution, so that, whatever might be the degree of concentration, a constant value was found for $[\alpha]$. Having obtained the same result with mixtures of oil of turpentine and ether, he was led to conclude that the rotation of an optically active substance when dissolved in an inactive liquid is directly proportional to the quantity of active substance in solution. Subsequently, however, Biot, along with other observers, found that his conclusions did not hold for other substances, such as, for instance, aqueous solution of tartaric acid, which showed an increased rotation in proportion as its solution became more dilute. During the last few years much attention has been given to this subject by various observers (reference to which will be made later on), and by whom the later observations of Biot with regard to tartaric acid and other substances have been fully confirmed. Nevertheless, it is still a common belief that all optically active substances behave essentially like cane sugar, and that the optical examination of a substance is complete when the deviation caused by any given solution has been observed and the specific rotation calculated therefrom by the formula $[\alpha] = \frac{100\,\alpha}{l.c}$. It will, therefore, be readily seen that the specific rotatory power deduced from observations of one particular solution of a substance can only hold good for that particular degree of concentration of that solution.

The specific rotatory power of any active liquid can, however, be determined directly, and is constant for any given temperature; but when such a liquid—as, for instance, oil of turpentine—is mixed in different proportions with an indifferent liquid, as alcohol, and from the composition, density, and angle of rotation of the resulting solution the specific rotation is computed, the values so obtained will differ in a greater or less degree from that of the pure substance. Hence it follows that the specific rotatory power of a substance is in some way influenced by the presence of inactive molecules, so that its value is altered somewhat, in the majority of cases, however, suffering an increase for increased proportions of the volume of solvent employed.

If, however, the active substance be a solid, its rotatory power can only be examined in solution, and then different values for $[\alpha]$ will be obtained according to the character of the solvent, none of which is the actual specific rotation of the pure substance but a value modified by the presence of the inactive liquid, and differing from the real value by a quantity unknown. When a pure homogeneous liquid is employed as solvent, so that only inactive molecules of one kind are allowed to influence those of the active substance, the variations in specific rotation are best shown by the graphic method, the percentages of inactive solvent q being taken as abscissæ, and the corresponding values of $[\alpha]$ as ordinates. The increase or decrease of specific rotation will then, in many cases, appear as a straight line, increasing, therefore, in direct proportion to q. Hence it may be expressed by the formula

$$[\alpha] = A + Bq,$$

in which the constants A and B must be ascertained from direct experiment. In other cases it will appear as a curve, usually a portion of a parabola or hyperbola, when the relation between the specific rotation and q is represented by an expression of the form:

$$[\alpha] = A + Bq + Cq^2, \text{ or } [\alpha] = A + \frac{Bq}{C+q}.$$

In these formulæ A denotes the specific rotation of the pure substance. The values B and C represent the increase or decrease of A for 1 p.c. of inactive solvent.

If $q = 0$, the specific rotation is that of the pure substance.

If $q = 100$, $[\alpha] = \infty$, hence the active substance vanishes and the solution consists of the inactive solvent alone; the rotatory power will then necessarily be *nil.*

In such active liquids as are miscible in all proportions with some other indifferent liquid the variations in the specific rotation up to extreme degrees of dilution can be determined by direct experiment, and the complete curve can be drawn from $q = 0$ to $q = 100$.

When, however, the active substance is a solid, the true specific rotation cannot be determined directly, and only a portion of the curve can be constructed, larger or smaller according to the solubility of the substance, but always commencing at some distance from the origin of the co-ordinates. Hence the value for $[\alpha]$, calculated from a solution of an active substance, is never the true specific rotation of the substance itself in a state of purity.

It is necessary first to ascertain the law of the variation brought about by the inactive liquid by examining a number of solutions of different strengths, and the true specific rotation may be approximately obtained by calculating the value of the constant A from the above formulæ.

The specific rotatory power of a substance not only varies with different degrees of concentration, but also varies according to the nature of the solvent. Thus the specific rotatory power of tartaric acid rapidly diminishes when acetone is added to the aqueous solution, and an aqueous solution of tartaric acid which was originally dextrorotatory may be made lævorotatory by the addition of butyl alcohol. In like manner the rotatory power of asparagine and aspartic acid can be changed from lævo- to dextro- by the addition of acetic acid.

Invert sugar, which becomes optically inactive at about 87°–88°C. in aqueous solution, loses its opticity in an alcoholic solution at 38°C. (Landolt, B. 13, 2329; Pribram, M. 9, 485). If dextro- tartaric acid be dissolved in methyl or ethyl alcohol, or in acetone, it becomes almost inactive.

When an active substance is brought in contact with more than one inactive substance in solution—as, for instance, when cane sugar is dissolved in a mixture of magnesium chloride and water, or when certain of the alkaloids are dissolved in a mixture of alcohol and chloroform—the determination of the specific rotatory power becomes somewhat complicated, as each of the inactive substances exerts its own influence on the true specific rotatory power, which therefore alters with every variation in the relative proportions of each inactive substance.

In the case of cane sugar, Farnsteiner (Ber. 23, 3570) found that solutions of the chlorides of magnesium, calcium, barium, and strontium tend to lower the specific rotatory power. The greater the amount of salt present the more is the rotation lowered, and, other things being equal, the lowering is greater the less the molecular weight of the salt—*i.e.* the depression is inversely proportional to the molecular weight; this is seen very clearly in the following table:—

Table III. *Effect of increasing amounts of salts whilst the proportion of sugar to water remains constant.*

Salt	Parts by weight of salt to 1 part by weight of sugar and 8·643 parts by weight of water	Density $\frac{17\cdot5^\circ}{4^\circ}$ Water at 4°C. = 1,000	$[\alpha]_D$
$MgCl_2$	0·000	1040·4	66·74
	1·670	1168·6	64·31
	3·267	1269·3	62·24
	3·948	1307·5	61·47
$CaCl_2$	1·719	1177·8	64·50
	2·998	1264·3	63·41
	3·646	1303·6	63·23
$BaCl_2$	1·40	1167·5	65·40
	2·250	1231·5	64·68
	3·794	1356·7	63·74
$SrCl_2$	0·954	1127·1	66·30
	2·622	1267·7	66·08

The specific rotatory power of active substances in solution is found to vary very much in some cases with increase or decrease in temperature. This is notably the case with lævulose and invert sugar, the specific rotatory powers of these substances decreasing very considerably as the temperature of their solutions is raised; whilst tartaric acid, on the contrary, shows an increase of rotation with increase of temperature. Thus, according to Jungfleisch and Grimbert (C. R. 108, 114), $[\alpha]_D$ for lævulose, which at 0°C. is 101·22, at 20°C. is only 90·02.

It is, therefore, most important that in all observations of the specific rotatory powers of substances in solution a record should be made of
(*a*) the degree of concentration;
(*b*) sp.gr. at 15·5°C.;
(*c*) nature of solvent;
(*d*) temperature at time of observation.

7. *Birotation.* Another and rather peculiar form of variation of specific rotatory power occurs in the case of certain sugars. This is commonly known as birotation, and is exhibited in freshly-prepared solutions of dextrose, lævulose, maltose, and lactose. If an aqueous solution of any one of these sugars be made as quickly as possible in the cold, and its optical activity observed from time to time, it will be found to exhibit a gradually decreasing rotatory power, which, after a certain length of time, becomes constant. The following results of experiments made by Tollens and Parcus (Ann. 257, 160) show this very clearly:

Max. angle observed in		min.	Constant in	hrs.
Maltose	+118·75	6	+136·8	5
Dextrose	+105·16	5½	+52·5	6
Lævulose	−104·02	6	−92·25	35
Lactose	+ 82·91	8	+52·53	24
Galactose	+117·48	7	+80·3	6

As will be seen from the above, the decrease begins immediately after solution, and at ordinary temperatures stops at the end of about twenty-four hours. The change is brought about more rapidly by heat, a few minutes sufficing at the boiling temperature.

8. *Absolute specific rotatory power.* As has been already mentioned, the value for $[\alpha]$ calculated from a solution of an active substance

in an inactive liquid can never be regarded as the true specific rotatory power of the substance itself in a state of purity. Therefore, in order to arrive at what is known as the absolute specific rotatory power of a given substance, solutions of different strengths must be examined and the results carefully tabulated, from which the true specific rotatory power may be approximately obtained by calculating the value of the constant A in the formula $[\alpha] = A + Bq$, or $[\alpha] = A + Bq + Cq^2$.

In order to test the accuracy of this method, Landolt made a long series of investigations on various substances, for details of which the reader is referred to the original papers (A. 189, 241). Liquid substances, such as oil of turpentine, and nicotine, were chosen, the absolute specific rotatory power of which could be determined by direct polarisation of the liquid substance itself. A series of solutions of different strengths were then prepared, from the observed specific rotatory powers of which, the value of the constant A was determined, and the result compared with that obtained by direct observation.

In order to render this as clear as possible, the details of some of the experiments are here given.

Determination of absolute specific rotatory power of right-handed oil of turpentine, sp.gr. 0·91083. The value for $[\alpha]_D$ determined for the pure substance was + 14·147°.

The following mixtures were prepared:—

Number of mixture	Oil of turpentine p	Alcohol q	$[\alpha]$
I.	73·0927	26·9073	14·496°
II.	47·5121	52·4876	14·788°
III.	22·2443	77·7557	15·095°

Column 4 represents what is known as the apparent specific rotatory powers of solutions of oil of turpentine in alcohol, or the specific rotatory powers for solutions of known concentration; but it will be seen that these numbers differ materially from what is known as the absolute specific rotatory power. Representing these graphically, fig. 26 shows that the three points representing the above determinations lie almost exactly in a straight line, corresponding to the equation $A + Bq$. Now, to find A

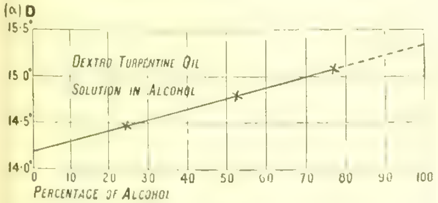


Fig. 26.

$[\alpha]_D = A + Bq$, $[\alpha]_{D_1} = A + Bq_1$, and $[\alpha]_{D_2} = A + Bq_2$;

whence $[\alpha]_D - [\alpha]_{D_1} = B(q - q_1)$ and $B = \frac{[\alpha]_D - [\alpha]_{D_1}}{q - q_1}$

whence from mixtures

$$\begin{aligned}
\text{I. and II. } A &= 14{\cdot}189, & B &= +0{\cdot}011415\\
\text{II. and III. } A &= 14{\cdot}150, & B &= +0{\cdot}012150\\
\text{I. and III. } A &= 14{\cdot}179, & B &= +0{\cdot}011780\\
\text{mean } A &= \overline{14{\cdot}173}, & B &= \overline{+0{\cdot}011782}
\end{aligned}$$

hence $[\alpha]_D = 14{\cdot}173 + 0{\cdot}011782q$. When $q = 0$ $[\alpha]_D = 14{\cdot}173$, which agrees very closely with the value found direct.

Various solutions of other liquid substances were examined in this manner by Landolt, and as the result of these investigations he deduced the following:

1. The rate of change in the specific rotation of an active substance, when progressively diluted with some inactive liquid, is gradual throughout.

2. The true rotatory power of an active substance can be calculated from observations on a number of its solutions. The greater the degree of concentration, the greater the possibility of the calculation being correct.

3. In calculating the true specific rotatory power of a substance, the same value is obtained whatever inactive liquid may have been used as solvent.

4. In making comparisons between solid bodies in respect to their rotatory powers, only those values should be used which hold good for the absolute substances—that is, only the constants A.

From these results a suitable method for determining the absolute specific rotatory powers of active solid substances can be arrived at. Solutions of a high degree of concentration should be employed. That inactive liquid in which the active substance is most soluble should be selected; at least three solutions of known different strengths should be prepared, and their respective rotatory powers observed. This done, the relations between the values for $[\alpha]$ and the percentage for solvent q are next represented graphically. By this means either a straight line or a curve is obtained. Where the three observations lie in a straight line, $[\alpha]$ being simply proportional to q, the value of the constant A may be calculated from the equation $[\alpha] = A + Bq$.

Should, however, the middle one of the three points diverge to either side of the straight line joining the other two, the result will be a curve. In such a case several other solutions of varying degrees of concentration will have to be made, so as to give a long series of observations, in order that sufficient data may be obtained for the construction of as full a curve as possible. For all practical purposes, the equation $[\alpha] = A + Bq + Cq^2$ will suffice to arrive at the value of the constant A. As an example, Landolt has applied this method to the determination of the absolute specific rotatory power of camphor.

Solutions of this substance in acetic acid, acetic ether, monochloracetic ether, benzene, dimethyl aniline, wood spirit, and alcohol were employed. All the solutions showed a decrease of specific rotation as the inactive solvent increased. With the exception of the two last-named solvents, the ratio of decrease in each case may be expressed graphically by means of a straight line, and hence for these solutions the formula $[\alpha] = A + Bq$ may be used. With wood spirit and alcohol, however, the decrease took the form of a curve, so that the formula $[\alpha] = A + Bq + Cq^2$ had to be applied.

The values of the constants A, B, and C may be found as follows:

$$(1)\ [\alpha]_{D_1} = A + Bq_1 + Cq_1^2$$
$$(2)\ [\alpha]_{D_2} = A + Bq_2 + Cq_2^2$$
$$(3)\ [\alpha]_{D_3} = A + Bq_3 + Cq_3^2$$

Subtracting 2 from 1 and 3 from 2:

$$[\alpha]_{D_1} - [\alpha]_{D_2} = B(q_1 - q_2) + C(q_1^2 - q_2^2)$$
$$[\alpha]_{D_2} - [\alpha]_{D_3} = B(q_2 - q_3) + C(q_2^2 - q_3^2),$$

whence $B = \frac{[\alpha]_{D_1} - [\alpha]_{D_2} - C(q_1^2 - q_2^2)}{q_1 - q_2}$; or this may be written $B = \frac{[\alpha]_{D_1} - [\alpha]_{D_2}}{q_1 - q_2} - \frac{C(q_1 + q_2)(q_1 - q_2)}{q_1 - q_2}$

$$\therefore\quad B = \frac{[\alpha]_{D_1} - [\alpha]_{D_2}}{q_1 - q_2} - C(q_1 + q_2).$$

Similarly $B = \frac{[\alpha]_{D_2} - [\alpha]_{D_3}}{q_2 - q_3} - C(q_2 + q_3)$; whence

$$C = \frac{[\alpha]_{D_1} - [\alpha]_{D_2}}{(q_1 - q_2)(q_1 - q_3)} - \frac{[\alpha]_{D_2} - [\alpha]_{D_3}}{(q_2 - q_3)(q_1 - q_3)}.$$

In a similar way, and working independently of each other, Tollens (Ber. 10, 1405) and Schmitz in 1876 (Ber. 10, 1414) determined the absolute specific rotatory power of cane sugar. The result of their investigations went to show that cane sugar and a number of other substances possess a greater rotatory power when examined in dilute solutions than they do in strong, but the fact was then overlooked that as the strength of the solution is decreased so does the experimental error make itself more and more felt, and, as the apparatus then available was far inferior to that now obtainable, it was deemed expedient by Tollens in 1885 (Ber. 17, 1751) to repeat the experiments he had made in 1876 on cane sugar, with all possible accuracy. In the case of cane sugar, eleven solutions were used, of various degrees of concentration, containing from 1·1062 to 67·4507 p.c. of pure dry cane sugar, and of which 43 complete measurements were made, each one being the mean of twenty readings, as shown in Table IV.

Table IV. *Specific rotatory power of cane-sugar solutions for various degrees of concentration.*

Percentage composition	$[\alpha]_D$ observed	$[\alpha]_D$ calculated
1·1062	66·341	66·402
1·6767	66·499	66·410
1·9870	66·276	66·414
2·0435	66·429	66·415
3·0421	66·198	66·428
4·9850	66·450	66·451
6·8427	66·482	66·470
9·0014	66·458	66·489
9·8963	66·454	66·496
34·8717	66·397	66·426
67·4507	65·529	65·587

From these observations, the mean specific rotatory power of cane sugar for $[\alpha]_D$ was found to be 66·4, and, as will be seen, none of the determinations differ from this number by more than the error due to observation.

9. *Determination of specific rotatory power. Polarimeters.* It has been already stated that a solution of cane sugar possesses the power of deviating a ray of polarised light to a fixed and definite degree, and this property has been taken advantage of in the construction of various instruments for the purpose of quantitatively estimating the amount of that body in solution. Such instruments are called 'saccharimeters,' 'polariscopes,' or 'polarimeters,' and the process of estimating cane and other sugars by such instruments is termed 'saccharimetry' or 'polarimetry.'

Until within a comparatively recent period, the determination of cane sugar was the only use to which the polarimeter was applied. But as the optical properties of other bodies came to be studied and to be known, a wider field for its use has been opened up, so that at the present time the value of the polarimeter as an agent in the quantitative estimation of optically active substances, as a means of control to determinations made by other methods, and as an aid to original investigation, is fully acknowledged.

10. *Mitscherlich's polarimeter.* The simplest of all forms of polarimeter is that devised by Mitscherlich. This consists of two Nicol prisms inclosed in brass tubes, and placed one at each end of a bar of metal (see fig. 27). The polariser P is made to turn on its axis as required, and can be fixed in any desired position by means of a small screw clamp S. The tube, containing the analyser N, is also capable of rotating on its axis, and is furnished with a small arm for that purpose, as well as with an index which measures the amount of rotation upon a fixed graduated circle of brass, divided into degrees and minutes. The observation tube, containing the saccharine solution, is placed in the space between the polariser P and the analyser N. Homogeneous yellow light, such as

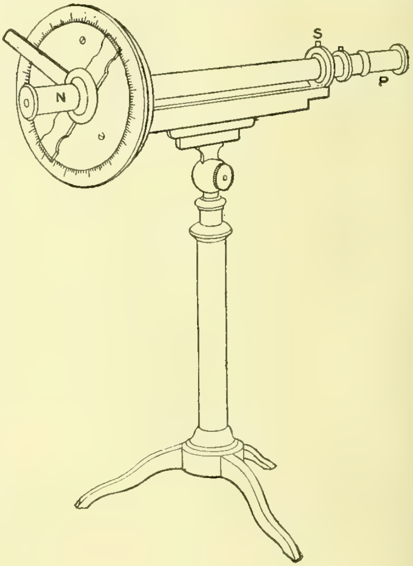


Fig. 27.

that obtained from a sodium flame, is used with this instrument, so that the angle a is determined for ray D.

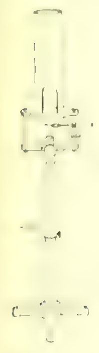


FIG. 28.

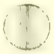
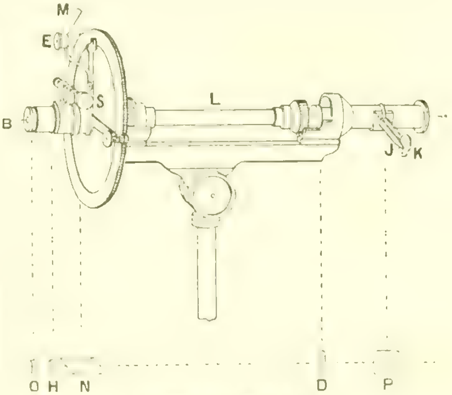


FIG. 29.

In using this form of polarimeter, the sodium lamp (fig. 28) is placed in front of the polariser at a distance of about an inch, in a darkened room. The zero point must first be determined. For this purpose the observation tube is filled with distilled water and placed in the instrument; the analyser is then turned until the index points to 0° on the scale, the small clamp at S is loosened, and the polariser P slightly moved backwards or forwards until the position for greatest darkness is attained. The appearance then presented will be a round disc (fig. 29), with a vertical dark band in the middle getting gradually lighter towards the sides, and this band must be brought, by means of the polariser, exactly into the middle of the field. The clamp S is then screwed up tight, and the instrument is set to exact zero. On now rotating the analyser towards the right, this disc becomes gradually lighter and lighter until 90° is reached. It will then have attained its maximum degree of illumination, and on continuing the rotation the disc gradually becomes dark again, so that at 180° the same appearance is presented as at 0°. It will, therefore, be seen that there are two positions for maximum darkness, 0° and 180°, and two positions for greatest illumination, 90° and 270°. If, then, while the instrument is set to 0° so that the period of maximum darkness obtains, the tube filled with a solution of cane sugar be placed in its proper position between the polariser and the analyser, the field of vision will appear bright owing to the deviation of the polarised ray by the sugar solution, and the analyser must be moved towards the right until the same appearance of maximum darkness again obtains. If now the number of degrees and minutes be read off on the graduated circle, this will be the amount of deviation caused by the sugar solution. Mitscherlich's apparatus is very rarely, if at all, used now, being replaced by more accurate forms of polarimeter. Of these the principal ones in use at present are Wild's polaristrobometer and Laurent's polarimeter, or polarimètre à pénombre, as it has been termed by the inventor. These give the rotation for ray D, whilst the Soleil-Duboscq and Soleil-Ventzke-Scheibler instruments are used for the transition tint.

11. *Wild's polarimeter.* This instrument, which has come more or less into use in some parts of the Continent, is a very great improvement on Mitscherlich's form, and depends upon the production of what are known as the bands of Savart. These bands are produced by the introduction of a prism, known as Savart's prism, consisting of two pieces of quartz cut obliquely and crossed over one another, between the polariser and analyser (which in this instrument has a rotatory movement), whereby a number of parallel black bands are brought into view in a dark field, and which vanish in certain positions of the polariser. The disappearance and reappearance, then, of these bands determine the amount of deviation. A sodium flame is employed as the source of light. For fuller details of this instrument, the reader is referred to Landolt's 'Handbook of the Polariscope,' English ed., p. 107.

12. *Laurent's polarimètre à pénombre.* Perhaps the most popular, as well as the most accurate, and best of all polarimeters is some one form or other of the type known as half-shade instruments or polarimètres à pénombre, and, of these, that form devised by Laurent is undoubtedly the best. The characteristic feature of half-shade instruments is that the circular field of vision appears divided into two halves, which for a certain position of the analyser appear one half dark and one half light, whilst for another position the whole field assumes a uniformly illuminated shade—neither dark or light, without a trace of the vertical line—and this position, which can readily be determined with the greatest accuracy, is taken as the zero point. When, then, a tube containing sugar solution is introduced, the position of equilibrium is disturbed; and the hitherto equally illuminated field of vision appears one half dark the other half light. The analyser has, therefore, to be turned to the right until an equally illuminated field again appears. This is the measure of the rotation produced by the sugar solution.



FIGS. 30 and 31.

The principle of construction of the Laurent polarimeter is shown in figs. 30 and 31.

In this instrument the monochromatic yellow light from a sodium lamp passes through the following optical arrangements:—

A thin plate cut from a crystal of bichromate of potash, and inclosed between two glass plates fixed in a movable diaphragm. This serves to free the yellow ray from intermixture of green, blue, and violet light. When, however, the solution under examination is more or less coloured, this plate may be dispensed with.

P, a double calc spar prism fixed in a movable brass tube, to which is affixed a lever K. This tube fits rather tightly into an outer tube carrying a bar or pointer J which passes between the stops on K, and so limits the amount of movement of the polariser P.

D, a circular diaphragm covered by a plate of glass, to which is affixed a thin plate of quartz, cut parallel to its axis, and just large enough to cover exactly one-half of the circular aperture. The thickness of this quartz plate must be so regulated that the yellow rays polarised parallel and perpendicularly to the axis may in their transmission undergo a retardation of half a wave-length.

L, the solution tube.

N, the analysing Nicol.

O and H, lenses forming together a small telescope.

The analyser is fixed in a stout brass tube carrying the vernier, and is capable of being rotated by means of a pinion round a graduated disc, which is fixed, and furnished with bevelled teeth in which the pinion works. The Nicol N is also capable of slight movement in its case by means of the screw S, so as to alter the zero point. The magnifier E furnished with a mirror M enables the observer to read the divisions of the scale more easily.

The distinguishing characteristic of Laurent's instrument is the half-wave plate of quartz cut parallel to the axis. This arrangement is shown in fig. 32, which represents the diaphragm of glass, the left half of which is seen to be covered with the plate of quartz, the axis of which is parallel to the line of division O A, whilst the right half, which is not so covered, allows the polarised ray to pass through it. Now let the polariser be so arranged that the plane of polarisation of the transmitted ray be parallel to the axis of the plate, that is, to O A. If then the analyser be turned so as to pass successively from total extinction to maximum degree of illumination, the two halves of the field of vision will always appear equally dark or equally light. If next the polariser be slightly inclined to O A at an angle α, so that the plane of polarisation of the rays passing through the uncovered half of the diaphragm may be represented by O B, it will be found that the plane of polarisation of the rays passing through the quartz plate will take the direction O B′, making an angle α' in the opposite direction and equal to α. If now the polariser be fixed in this position, and the analyser be turned in the direction S P, so that its principal section S P is perpendicular to O B, total extinction will take place on the right side, so that this half will appear dark while only partial extinction takes place on the left side, and accordingly this will appear more or less light, as shown in fig. 33. If, on the other hand, the analyser be turned in the direction S′ P′, just the reverse will occur, as seen in fig. 34. In the middle position—that is, when the principal section S P of the analyser is perpendicular to O A—there will be only partial extinction in the two halves, so that a uniform shade of equal intensity will be observed in both (fig. 35). The slightest movement, however, of the analyser, either to the right or left, will at once destroy this equality. The same phenomena are observed when the analyser is moved through an angle of 180°. This position of uniform shade is made the zero point of the instrument, and the smaller the angle α which the plane of the polariser P makes with the axis of the quartz plate O A the greater will be the degree of shade, and the more sensitive will the instrument become. This slight movement of the polariser is allowed for by means of the lever K (fig. 31), whereby the field of vision can be rendered lighter or darker according to the nature of the solution. So that with this type of instrument darker solutions can be observed than would be possible with those of the transition tint.

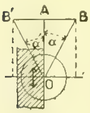


FIG. 32.

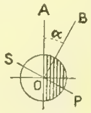


FIG. 33.

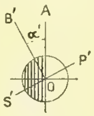


FIG. 34.

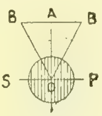


FIG. 35.

To set the instrument to zero, the divided diaphragm is first brought into focus by means of the telescopic eyepiece, so that the edge of the quartz plate appears as a sharply defined vertical line. The analyser is then turned until both halves of the field of vision appear equally dark. The polariser is next fixed in that position whereby the least movement of the analyser destroys this equality of shade.

Having adjusted the polariser and introduced the observation tube filled with distilled water, the analyser is moved either to the right or left until the index of the vernier exactly coincides with zero on the graduated circle. If, then, an equally uniform shade is observed all over the divided disc, which is destroyed by the slightest movement of the analyser, the instrument is correct; if not, the screw S must be turned backwards or forwards until both halves of the disc are equally illuminated.

13. *Transition tint instruments.* Instruments of this class are constructed expressly for determining the percentage of sugar in solutions of known density, and are known more particularly as saccharimeters. They differ essentially in construction from the forms of polarimeter just described; the graduated circle being replaced by a scale divided into 100 equal parts, or degrees, each division representing one p.c. of cane sugar. The optical parts also are different, and their construction is based upon the following facts discovered by Biot:

1. That when a polarised ray is transmitted through several media possessing rotatory power in different directions, their separate activities may become either partially or wholly neutralised, according to the lengths of the media.

2. That the rotatory dispersion of cane sugar is the same as that of quartz.

The earliest form of these instruments was that devised by Soleil in 1848. This has been much improved upon by Duboscq, and in its present form is known as the Soleil-Duboscq saccharimeter, a general view of which is shown in fig. 36, whilst the optical parts are seen in fig. 37. These are as follows :—

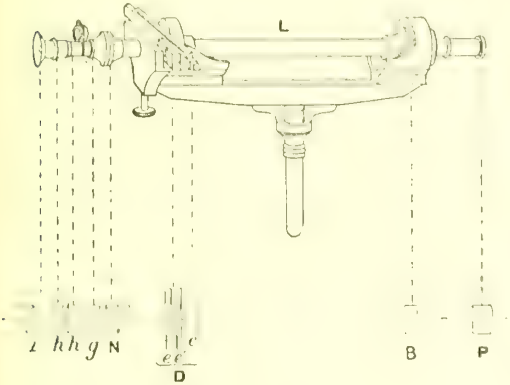
P, the polariser, consisting of an achromatised calc-spar prism, arranged with its principal section vertical.

B, a plate of quartz, called the plate of double rotation or bi-quartz, composed of two halves of equal thickness cut perpendicularly to the axis of crystallisation, and fitted accurately together, so that the line of junction is vertical. These half-discs, which may be either 3·75 mm. or 7·5 mm. thick, have different rotations, the one being left-handed and the other right-handed.

L, the solution tube.

D, the so-called rotation compensator.

This consists of a plate of quartz *c*, usually right-handed, and two wedge-shaped quartz plates *e e′*, both having the same left-handed rotation. These plates are each fixed in a brass frame, and, by means of a rack and pinion, are made to slide over one another, so that their combined thickness may be made either equal to, greater, or less than that of *c*. The distance moved to effect any particular adjustment is shown by a graduated scale attached to the brass frame.



Figs. 36 and 37.

N, the analyser, which may consist of an achromatised calc-spar prism; its principal section must be arranged parallel to that of the polariser P, when the thickness of the bi-quartz B is 3·75 mm. and perpendicular thereto when the thickness is 7·5 mm.

Soleil introduced an extra Nicol prism, shown at *i*, and a plate of quartz, *g*, ground perpendicular to the axis, fixed in a movable case, and which may be turned at will through an angle of 180°. This arrangement is called the regulator, and is used for the purpose of counteracting, to a certain extent, the influence of the colouration in the liquids subjected to examination, and to restore the sensitive tint which would otherwise be destroyed when using such coloured liquids.

h i is a small Galilean telescope.

In order to understand the action of the several parts, let the instrument be so arranged that light passes only through the polariser and analyser. These are arranged with their principal sections parallel so that the field is at its maximum of illumination.

Let the active bi-quartz B be interposed between P and N; the white light coming from P will be rotated and decomposed into its component coloured rays. Of these emergent rays those whose plane of polarisation is at right angles to that of the analyser will not be transmitted, and should these be the yellow rays, the remainder will in transmission combine to a pale lilac tint, which, with the slightest alteration of the plane of polarisation, passes into pure red or pure blue. This intermediate colour is the transition tint.

If now the combination D, known as the rotation compensator, be put in its place, the quartz wedges *e e′* being so adjusted that their combined thickness is exactly equal to that of the plate *c*, as the rotatory powers of *c* and *e e′* act in exactly opposite directions they neutralise each other and the sensitive tint still prevails. This position of the wedges corresponds with the zero point of the scale. If now a tube containing a solution, say, of cane sugar, be interposed, the uniformity of colour between the two half discs is immediately destroyed, appearing differently coloured, green and blue predominating in one, red and orange in the other; by sliding the quartz wedges so as to produce rotation opposite to that of the solution, a position may be found where the action of the latter is neutralised, and this will be indicated when the halves of the field of vision again exhibit uniformly the sensitive tint.

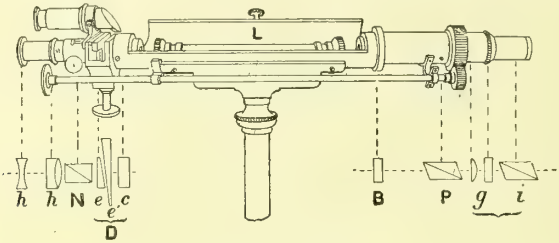
This action of the compensator shows not only whether the solution of the substance examined is right- or left-rotating, but also the degree as measured by the thickness of quartz necessary to neutralise the deviation of the body examined. The latter is measured by means of a graduated scale fixed to one of the slides, while upon the other is a small vernier serving as an indicator.

The Soleil-Ventzke-Scheibler saccharimeter, in the principles of its construction, is identically the same as the Soleil-Duboscq, but the mechanical parts have been greatly improved and the optical arrangement slightly altered.

These alterations were made in Germany by Ventzke, who introduced a different scale, the mechanical improvements being made by Scheibler. The various parts as shown in figs. 38 and 39 are lettered respectively the same as the Soleil-Duboscq, so that the description there given will apply equally to the Ventzke, the principal difference being that in the Soleil-Duboscq both the quartz plates *e e′* of the compensator are movable, whereas in the Ventzke-Scheibler one of them is fixed and has the scale attached to it, whilst the other is movable and carries the vernier.

In order to test the correctness of this instrument, it is placed in front of a paraffin or argand gas lamp in such a position that the maximum amount of light may pass through. The 200 mm. tube is filled with distilled water and placed in the instrument, and the eye-piece of the telescope moved in and out until the line dividing the bi-quartz appears well defined; if, then, the halves of the disc differ in colour, the milled head is turned one way or other until the colours of both halves appear to be perfectly identical. The regulator is next turned until the sensitive tint is obtained, which, with the slightest movement backwards or forwards of the movable quartz wedge, produces a difference in colour of the two half discs. The best tint to work for is that which most nearly approaches to white, as the paler the tint is the more easily is it displaced by the movement of the quartz wedge. Having fixed upon the sensitive tint, the quartz wedge is next moved backwards and forwards until the same tint is obtained. This ought to be done several times; should, then, the zero on the vernier be found not to coincide exactly with the zero on the scale, the screw must be turned until it does.

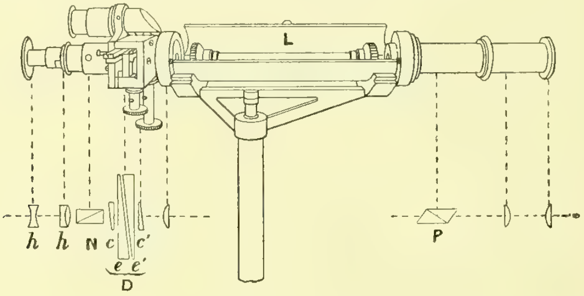
Should it, however, be impossible to obtain a uniform tint on both halves of the field, the polariser and analyser are not in perfect adjustment. In order to make them so, the movable and fixed quartz wedges *e e′*, as well as the compensation plate *c*, are removed, the cover closed down, and the analyser turned by means of the screws until uniformity of tint in both halves is obtained. The quartz wedges and plate are again fixed in their places, and the zero point determined as before.



Figs. 38 and 39.

The tube is then taken out and replaced by a tube filled with sugar solution. The uniformity of tint is immediately destroyed, and the quartz wedge must be moved until the colour of the two halves again coincides in tint. If the solution be at all coloured this tint will have a slightly yellowish tinge. In this case the screw of the regulator must be turned a little to the right or left until the same tint be obtained as before. Several readings are then taken, and the mean of them recorded. The transition tint instrument can only be used by persons who have a sufficiently keen appreciation of colour to be able accurately to determine the transition tint, and even amongst such persons, with different observers the colour of the sensitive tint will vary to a slight extent, so that each observer must determine for himself the exact zero point according to his own idea of sensitiveness of tint. As has been already stated, if the solutions be at all coloured, the extra Nicol has to be used so as to neutralise to a certain extent the yellowish tinge imparted to the field of vision. This, of necessity, has the effect of cutting off a certain amount of light, as well as diminishing the sensitiveness of the instrument somewhat.

It is almost needless to remark that for colour-blind persons the transition tint instruments are useless.



Figs. 40 and 41.

14. *Schmidt and Haensch's half-shadow saccharimeter.* This instrument (figs. 40 and 41)—which in its general form and appearance is almost exactly like the Ventzke-Scheibler, though differing somewhat in its optical parts—has within the last few years come into very general use as a saccharimeter. It shows a divided disc of a uniformly yellowish grey colour when set at zero, the halves rapidly changing to dark or light, like the Laurent, when an optically active substance is introduced. On the other hand, it carries the saccharimetric scale showing percentage of sugar like the Ventzke-Scheibler, and is used with ordinary lamp-light instead of monochromatic. The various parts of the instrument, as shown in fig. 41, are very similar to those of the Ventzke-Scheibler, the exception being the arrangement of the so-called compensating system.

For whereas in the transition-tint instruments a pair of quartz wedges and a compensation plate are necessary, the same object is attained in this instrument by means of two pairs of quartz wedges, the compensation plate *c*, fig. 37, being replaced by a pair of quartz wedges *cc'*, fig. 41, of exactly similar proportions to the first pair, but having an opposite rotation. One of these pairs of wedges is immovably fixed in the instrument, whilst the other is horizontally movable at right angles to the axis. By such an arrangement the instrument is rendered extremely sensitive, and it is claimed by the inventors that much closer readings can be obtained than with the Soleil-Ventzke-Scheibler. The following instructions for using this instrument have been issued in the Report of the United States Internal Revenue Department as to standards and methods for the polarimetric estimation of sugars:

In using the instrument the lamp is placed at a distance of at least 200 mm. from the end; the observer seats himself at the opposite end in such a manner as to bring his eye in a line with the optical axis of the instrument. The telescope is moved in or out until the proper focus is secured, so as to give a clearly-defined image, when the field of the instrument will appear as a round, luminous disc, divided into two halves by a vertical line passing through the centre, and darker on one half of the disc than on the other. If the observer, still looking through the telescope, will now grasp the milled head and rotate it, first one way and then the other, he will find that the appearance of the field changes, and at a certain point the dark half becomes light, and the light half dark. By rotating the milled head delicately backwards and forwards over this point he will be able to find the exact position of the quartz wedge operated by it, in which the field is neutral, or of the same intensity of light on both halves.

The three different appearances presented by the field are best shown in fig. 42.

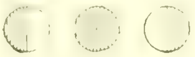


FIG. 42.

With the milled head set at the point which gives the appearance of the middle disc as shown above, the eye of the observer is raised to the reading tube, and the position of the scale is noted. The scale proper is attached to the quartz wedge, which is moved by the milled head, whilst attached to the other quartz wedge is the vernier, which is fixed, and which serves for the exact determination of the movable scale with reference to it. On each side of the zero line of the vernier a space corresponding to nine divisions of the movable scale is divided into ten equal parts. By this means the fractional part of a degree indicated by the position of the zero line is ascertained in tenths; it is only necessary to count from zero until a line is found which makes a continuous line with one on the movable scale.

With the neutral field as indicated above, the zero of the movable scale should correspond closely with the zero of the vernier, unless the zero point is out of adjustment.

If the observer desires to secure an exact adjustment of the zero of the scale, or in any case if the latter deviates more than one half of a degree, the zero lines are made to coincide by moving the milled head and securing a neutral field at this point by means of a small key which fits into a nipple on the left hand side of the fixed quartz wedge of the compensating system. The nipple is turned one way or the other until the field is neutral. Unless the deviation of the zero be greater than 0·5°, it will not be necessary to use the key, but only to note the amount of the deviation, and for this purpose the observer must not be content with a single setting, but must perform the operation five or six times and take the mean of these different readings. If one or more of the readings shows a deviation of more than 0·3° from the general average, they should be rejected as incorrect. Between each observation the eye should be allowed ten to twenty seconds of rest.

The setting of the zero having been performed as above, the determination of the accurate adjustment of the instrument by means of the control quartz plates is proceeded with. Three such plates are furnished with each instrument, which have sugar values respectively approximating 80°, 90°, and 100°.[1] These values may vary with the temperature, and tables are furnished with them which give their exact values at different temperatures from 10° to 35°C.

One of these plates is placed in the instrument, and the field observed; it will be seen that the uniform appearance of the field is changed. The milled head is turned to the right until the exact point of neutrality is re-established, just as described above in setting the zero. The scale is read, the observation repeated, the reading taken again, and so on until five or six readings have been made. The average is taken, readings being rejected which show a divergence of more than 0·3, and the result corrected for the deviation of the zero point, if any was found, the deviation being added if it was to the left, and subtracted if to the right. If the adjustment of the instrument be correct, the result should be the value of the control plate used, as ascertained from the table, for the temperature of 20°. Each of the three plates is read in the instrument in this way. A variation of 0·3 from the established values may be allowed for errors of observation, temperature, &c., but in the hands of a careful observer a deviation greater than this with one of the three plates after a careful setting of the zero shows that the instrument is not accurately adjusted.

The complete verification of the accurate adjustment of the polariscope by means of three control plates, as given above, should be employed whenever it is set up for the first time by the person using it, whenever it has sustained any serious shock or injury, and whenever it has been transported from one place to another. It should also be done at least once a week while the instrument is in active use.

After the complete verification has been performed as described, further checking of the instrument is done by means of one control plate alone, the one approximating 90°, and the setting of the zero point is dispensed with, the indication of the scale for sugar solutions being corrected by the amount of deviation shown in the reading of the 90° control plate from its established value as ascertained from the table, at the temperature of the room.

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[1] [illegible]

For example: A sugar solution polarises 80·5; the control plate just before had given a polarisation of 91·4, the temperature of the room during both observations being 25°C. According to the table, the value of the control plate at 25°C. is 91·7; the reading is, therefore, 0·3 too low, and 0·3 is added to the reading of the sugar solution, making the corrected result 80·8. The temperature of the room should be ascertained from a standardised thermometer placed close to the instrument, and in such a position as to be subject to the same conditions.

15. *Construction of the saccharimetric scale.* In the transition tint, as well as in Schmidt and Haensch's latest form of half-shadow instruments, the graduated scale does not give measurements in angular degrees, but is reckoned in divisions, and is constructed thus:—

For the Ventzke-Scheibler saccharimeter a tube 200 mm. in length, and filled with an aqueous solution of pure cane-sugar, having at the temperature of 17·5°C. a specific gravity of 1100 (water = 1000), is placed in the instrument, and the point observed which gives the exact neutral tint. This point is marked as 100 on the ivory plate, and the space between this and the zero point is then divided into 100 equal parts, the graduation being also extended some way to the left and right of these two points respectively. It has been found by careful experiments that a solution of the above specific gravity contains in 100 c.c. exactly 26·048 grms. of sugar. Hence if this weight of pure dry cane sugar be taken and made into a solution of 100 c.c. and polarised, the reading will be the same as if the solution were prepared according to normal density.

Each division, therefore, of Ventzke's scale indicates a value of 0·26048 grms. of sugar per 100 c.c. of solution. Accordingly, to determine the concentration c (grms. of sugar per 100 c.c.), a 200 mm. tube is filled with the solution, the deviation produced by it on the scale read off, which, multiplied by 0·26048, gives c.

When the specific rotatory power of a substance has to be determined with this form of polarimeter, it is necessary first to convert the reading observed as divisions into degrees of angular measurement, and then proceed to calculate the specific rotatory power by means of equation IV. section 18. Taking the value of $[\alpha]_j$ for cane sugar as 73·8, O'Sullivan finds that 100 divisions of the Ventzke scale are equal to 38·4° $[\alpha]_j$—that is to say, that a solution containing 26·048 grms. of cane sugar per 100 c.c., and which produces a rotation of 100 divisions on the Ventzke scale, would record on instruments having angular graduation a rotation for the same ray through an angle of 38·4°; hence one division of the Ventzke scale equals ·384° angular measurement.

Therefore, in order to calculate the specific rotatory power from observations made with this instrument, equation IV. becomes

$$[\alpha]_j = \frac{38{\cdot}4\alpha}{2c}.$$

In the Soleil-Duboscq instrument the scale is so constructed that the 100 point is recorded by a solution in a 200 mm. tube, containing 16·35 grms. of pure cane sugar per 100 c.c.; consequently, each degree of the scale represents 0·1635 grms. of sugar per 100 c.c.

According to O'Sullivan, 100 divisions of this instrument correspond to 24° for the mean yellow ray; hence one division of this scale equals 0·24 angular degrees, ray j—whence equation IV. becomes

$$[\alpha]_j = \frac{24\alpha}{2c}.$$

16. *The Vernier scale.* In most instruments the scale is divided into tenths, and in reading it the number of whole divisions counting from the zero point is first read off, and then the decimal parts of a division by means of the vernier, the principle of which is as follows:—

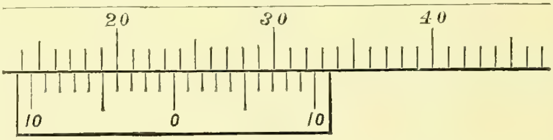

FIG. 43.

A length equal to 9 divisions on the scale is marked off on the vernier, and this length is then divided off into 10 equal parts, reading from 0 up to 10 in the same direction as the scale, so that the length of a division on the vernier is to that of a division on the scale as 9 to 10. Each division on the vernier is equal to $\frac{9}{10}$ths of a division on the scale. If, therefore, any two divisions, one on each scale, coincide or are in a line with each other, the next pair of divisions to these will differ from a like coincidence by a quantity exactly equal to $\frac{1}{10}$th of a division. Similarly, the next pair will show a difference of $\frac{2}{10}$ths of a division, and so on. Thus in fig. 43, the sixth division on the vernier coincides with the twenty-ninth division on the scale. A little consideration will show that the two divisions immediately preceding them (fifth on vernier and twenty-eighth on scale) do not exactly coincide, and that the deficiency of coincidence between these two lines is the $\frac{1}{10}$th of a division. Proceeding to the two figures in front of these it will be seen that their deviation from coincidence is $\frac{2}{10}$ths of a division. In like manner the next pair are vertically distant from each other $\frac{3}{10}$ths of a division—and in regular succession 2 and 25, 1 and 24, 0 and 23 form couples which deviate from coincidence respectively $\frac{4}{10}$ths, $\frac{5}{10}$ths, and $\frac{6}{10}$ths of a division. As, therefore, the 0 on the vernier is distant $\frac{6}{10}$ths of a division from the point of coincidence, and as the line on the scale at such point of coincidence is the 29th, 6 from 29 gives 23, the number of whole divisions to be read off, to which is to be added 0·6, the number of divisions on the vernier, counting from its zero to the point of coincidence. 23·6 is therefore the number to be read off, as shown in fig. 39.

The vernier can be equally well applied to circular divisions, and to such instruments as are employed in the measurement of angles. In such cases the vernier is a segment of a circle which is concentric with the segment of the circle forming the scale, but in this case a degree of the circle is neither divided into 10ths nor 100ths, but into 60ths, 60 minutes being equal to 1 degree, and hence the vernier, instead of being arranged according to the decimal system, as in the case of rectilinear measurement, must be regulated according to the sexagesimal system. Thus in the case of the Laurent polarimeter the circle is divided into degrees and half degrees, and to this is attached a vernier so graduated that fifteen of its divisions are together equal to fourteen of those on the circle. A division of the former, therefore, is $\frac{1}{15}$th smaller than a division of the latter, and by this means can be measured $\frac{1}{15}$th of $\frac{1}{2}$ or $\frac{1}{30}$th of a degree, which is equal to 2 minutes—or, as it is generally expressed, 0° 2′.

The construction of the saccharimeters mentioned in sections 13 and 14 depends upon the fact that the dispersive power of solutions of cane sugar is the same as that of quartz; and, while this holds good for cane sugar, it does not necessarily follow that it should do so for all other optically active substances, and as a matter of fact it does not, for some which have been examined—cholesterin, for instance—so that in such a case the compensator fails to restore a perfectly uniform colour in the two halves of the disc. Therefore, in the case of all substances whose rotatory dispersion differs materially from that of quartz, it is advisable to employ one of those instruments on which the angle of rotation can be read off directly.

17. *Observation tubes.* The tubes used for observing the specific rotation of liquids or solutions are usually made of glass, which is either left uncovered or fixed within a simple brass tube. The one most commonly employed measures 200 mm. in length, but the 100 mm. tube is often used, more especially when dealing with highly-coloured solutions. These are the two sizes always used for technical work, but for original investigations larger sizes, 300 mm. and upwards, are frequently employed. The internal diameter varies from 6 to 10 mm., whilst the thickness of the glass sides is about 2 mm.; the ends, which are ground flat and exactly perpendicular to the sides, are closed by plane parallel glass plates, which form a liquid-tight joint and are kept in position by means of brass screw caps, perforated in the centre, fitted with washers of indiarubber, and fixed on to the end of the tube. Care should be taken not to screw these caps on too tightly, owing to the tendency of the glass plates under pressure to become double refracting, so that the light passing through them is circularly polarised. Other circumstances apart from pressure—such as imperfect annealing, &c.—may exert a similar influence. All glass covers should, therefore, be tested before being used, and only those retained which show no circular polarisation.

In those cases in which the rotatory power of liquid substances or solutions is affected to any appreciable extent by changes of temperature, the observation tubes should be inclosed in a jacket of brass, through which a constant stream of water supplied from a reservoir at the desired temperature is allowed to flow.

Before filling the observation tube with the liquid under examination it must be thoroughly well dried by pushing through it a plug of filter paper or of cotton wool, or having closed one end of it with the cover glass and screw cap, it is filled and emptied twice in succession with the liquid to be polarised. The tube is then filled with the solution just to overflowing, and allowed to stand a few seconds to permit the air bubbles to rise. The cover glass, which must be perfectly dry, is then pushed slowly over the end of the tube in such a manner that the excess of liquid is carried over the side, whilst the cover glass exactly closes the tube, leaving no air bubbles in the tube, nor any of the liquid upon its upper surface. If any air bubbles should be left in, the cover glass must be removed, wiped perfectly dry, a little more liquid poured into the tube, and the cover glass replaced as before. The screw cap is then carefully screwed on over the cover-glass, and the outside of the tube wiped clean and dry. Care must be taken not to screw the cap on too tightly, and that no liquid adheres to the outsides of the cover glasses after the caps have been screwed on. The tube is then placed in position in the polarimeter, and the reading taken. Five or six readings should always be made, and the average of these taken as the correct one.

As will be readily seen, it is of the greatest importance that the length of the tube should be absolutely correct, and although it is essential for research work that the length should be verified by the observer himself, yet for all practical and technical purposes it is best left to the instrument maker.

18. *Specific Rotatory Powers of Active Substances.*—In determining the specific rotatory powers of various active substances the following factors have to be taken into account:

1. Name of ray used.
2. Nature of solvent.
3. Concentration of, or percentage composition of, solutions.
4. Temperature at which the angle of rotation has been observed.
5. The direction of rotation, + right-handed or − left-handed.

All the specific rotations given in this article refer to compounds the exact chemical composition of which is given by the formulæ annexed. As before $[\alpha]_D$, $[\alpha]_j$, denote respectively the specific rotation for ray D and for the transition tint j.

α denotes the angle of rotation for a layer of liquid 100 mm. thick.

c denotes concentration, *i.e.* the number of grms. of active substance in 100 c.c. of solution.

p denotes percentage composition, *i.e.* the numbers of grms. of active substance in 100 grms. of solution.

d denotes specific gravity of the solution.

t denotes temperature in degrees Centigrade at which the rotation has been observed.

In calculating the specific rotatory power by the equation $[\alpha]=\frac{10^4}{l.c.}$, let l = 1,000 mm. and $c=10$ grms. per 100 c.c., then this equation becomes $[\alpha]=\alpha$, that is to say, the angle observed in a 1,000 mm. tube of a 10 grm. per 100 c.c. solution is the specific rotatory power of that substance. This O'Sullivan defines as 'the angle through which the plane of polarisation of a given ray is rotated by passing through a layer 1,000 mm. in length of a solution containing 10 grms. dry substance in 100 c.c. of distilled water.'

In examining a substance the specific rotatory power of which is not known, the most convenient weight to take is 10 grms. of dry substance dissolved in water and made up to exactly 100 c.c.

In practice it is usual to take observations in a 200 mm. tube, and for $c=10$.

Equation III. then becomes

$$[\alpha]=\frac{10^4\alpha}{200c}.$$

and IV.

$$=\frac{100\alpha}{2c}.$$

Hence, in order to find the specific rotatory power of any active substance when in aqueous solution, we only require to know the values of α and c.

Now, α is the deflection caused by the solution in 200 mm. tube when observed in the polarimeter, and c can easily be found from the sp. gr. of the solution. for when 10 grms. of pure dry cane sugar are dissolved in water, and further diluted until the volume exactly measures 100 c.c., such a solution has been found to possess a sp.gr. of 1,038·6 (water = 1,000); hence 1 grm. of cane sugar per 100 c.c. has approximately a sp.gr. of 1,003·86. If, therefore, we determine the sp.gr. of any solution of cane sugar, and subtract from this gravity 1000, then divide the remainder by 3·86, we obtain the number of grms. per 100 c.c. of cane sugar contained in that solution. The sp.gr. of known solutions of other carbohydrates has also been determined; for instance, a 10 grm. per 100 c.c. solution of maltose shows a sp.gr. of 1,039·5. A similar solution of dextrin gives practically the same; whilst a solution of dextrose of same concentration gives a sp.gr. of 1,038·1 – 1,038·6. It will thus be seen that some carbohydrates in a 10-grm. per 100 c.c. solution show a slightly higher sp.gr. than cane sugar, whilst others give lower results. Since, therefore, the densities of the various carbohydrates in solution differ to a certain extent, it naturally follows that the determination of the concentration from the sp.gr. will be somewhat complicated when two or more such bodies are present in the solution.

In consideration of this fact, it has been deemed advisable to employ one constant and unvarying divisor for the determination of the solid matter per 100 c.c. in solution, and to which all specific rotatory powers may be referred.

The divisor for cane sugar, 3·86, has been adopted for this purpose, and is recognised by the symbols $[\alpha]_{D3\cdot86}$ and $[\alpha]_{j3\cdot86}$ respectively.

19. *Specific Rotatory Power of Cane Sugar* $C_{12}H_{22}O_{11}$. It has been already stated that Tollens, in repeating his experiments on cane sugar in 1884, found as the mean result of his observations the specific rotatory power of cane sugar to be 66·4 for $[\alpha]_D$.

This number only differs by ·1 from the value previously deduced by both Schmitz and Tollens for solutions of cane sugar of a mean concentration $c=14$. $[\alpha]_D=66\cdot5$, and for all practical purposes this latter number may be taken as correct.

For the transition tint O'Sullivan finds as the mean of several very carefully-conducted observations the value for $[\alpha]_j$ to be 73·8; therefore by determining once and for all the amount of deviation produced by a given solution of pure dry cane sugar of known concentration c in a tube of given length l, the number of grms. of sugar per 100 c.c. in any solution of unknown strength, or the percentage of sugar on the weight taken, can easily be calculated from a determination of the optical activity of such a solution.

20. *Specific Rotatory Power of Dextrose* $C_{12}H_{24}O_{12}$. A series of similar observations were made by Tollens on pure dextrose dried at 60 70°C. His results showed that, unlike cane sugar, the specific rotatory power of dextrose increases with the concentration, and on being represented graphically takes the form of a curve.

Table V.—*Specific rotatory power of solutions of dextrose for various degrees of concentration.*

No. of solution	Percentage composition p	$[\alpha]_D$ found	$[\alpha]_D$ calculated
4	1·4978	52·407	52·532
8	1·7933	52·289	52·537
2	2·0133	52·073	—
5	2·7533	52·370	52·556
9	7·6042	52·691	52·673
1	10·0272	52·433	—
7	10·0992	52·738	52·742
3	10·2567	52·636	52·747
6	17·5982	52·991	52·991

From these numbers is derived the formula $[\alpha]_D=+52\cdot50+0\cdot018796p+0\cdot00051683p^2$; for $p=9\cdot6823$, that is for $c=10$, $[\alpha]_D$ becomes $+52\cdot73$.

For the transition tint the rotation value for dextrose has been very accurately determined by C. O'Sullivan (C. J. 57, 835), who found it to be for $c=10$, $[\alpha]_j=57\cdot0°$.

21. *Specific Rotatory Power of Lævulose* $C_{12}H_{24}O_{12}$. The information respecting lævulose has been until recently very meagre, and to a certain extent unreliable, for what was already known badly needed confirmation. This was principally owing to the difficulty hitherto experienced in obtaining this carbohydrate in a state approaching to any degree of purity.

Dubrunfaut (C. R. 42, 901), who appears to be the first to have recorded any reliable observations on the specific rotatory powers of lævulose and invert sugar, found for lævulose obtained by means of the lime process from invert sugar the following values:

	14°C.	52°C.	90°C.
$[\alpha]_j$	–106.	–79·5.	–53.

Other values have been obtained by other observers, as under:

Neubauer (B. 1877, 829): $[\alpha]_D^{14°C.} = -100$.

Jodin (C. R. 58, 613): $[\alpha]_j = -104$.

Kiliani (B. 14, 2530): $c = 1$ to 4; $[\alpha]_D = -92°$.

In 1888, Hönig and Schubert succeeded in obtaining lævulose in a crystalline form from inulin.

In the same year, Herzfeld (A. 244, 274) and Winter (A. 244, 295) prepared crystalline lævulose from inulin, which they submitted to polarimetric observation.

Herzfeld found the specific rotatory power of pure lævulose at 20°C. to be only −77·81; and for a 20 p.c. solution at 20°, $\alpha_D = -70·59$.

Winter found for $\alpha_D^{20°C.} - 71·47$, $c = 20$.

Lævulose separated from invert sugar by Dubrunfaut's calcium method gave:

$$[\alpha]_D^{20°C.} = -73·54,\ c = 1·5.$$

Hönig and Jesser (M. 9, 562) have examined lævulose most carefully prepared by them from inulin, and find that, for the same degree of concentration (p), the increase and decrease in the specific rotatory power is proportional to the temperature, so that the relation can be expressed by the equation $\alpha_D^t = a + bt$. The values of a and b, calculated from two series of observations, in which $p = 9·0870$ and 23·4979 respectively, show that between these limits of concentration the rotation increases 0·67112° for every 1°C. From this relation the rotatory power of solutions containing various quantities of water (q) have been calculated, from which has been deduced the relation between the specific rotatory power and the percentage of water, and which may be be expressed by the equation:

$$[\alpha]_D = A + Bq.$$

Hence at 20°,

$$[\alpha]_D^{20°C.} = -113·9635 + 0·25831q.$$

The specific rotatory power of pure anhydrous lævulose at 20°C. is therefore −113·96; whilst for $c = 10$,

$$[\alpha]_D^{20°} = -90·716.$$

As the result of their experiments, the authors conclude that Herzfeld's results are incorrect, owing to the substance employed by him having been contaminated with dextro-rotatory inulin derivatives.

Jungfleisch and Grimbert (C. R. 107, 390) find that the rotatory power of freshly-prepared solutions of lævulose is greater than that of solutions which have been kept for some time.

A solution of lævulose containing 9·75 grms per 100 c.c. gave, 35 minutes after its preparation, $\alpha_D = -97·33°$ at 7 C.; 55 mins. after, $\alpha_D = -96·11$; 75 mins. after, $\alpha_D = -95·11$; 1 hr. 45 mins., $\alpha_D = -94·77$; after which it remained constant.

The specific rotatory power of lævulose diminishes by 0·56° for every 1°C. increase of temperature.

The specific rotatory power of lævulose in solution may be calculated by means of the following formula:

$$[\alpha]_D = -101·38 - 0·56t + 0·108(p - 10)$$

(p = concentration) for temperatures between 0° and 40°C., with concentrations less than 40 grms. per 100 c.c.; above 40°C. appreciable traces of lævulose are destroyed.

Jungfleisch and Grimbert, in a later communication (C. R. 108, 144), notice that the rotatory power of pure lævulose prepared from inulin varies considerably from the value obtained by calculation from the optical activity of invert sugar, this being considered as a mixture of equal parts of lævulose and dextrose; *e.g.* at 20°C. $[\alpha]_D$ for pure lævulose from inulin = 90·02; $[\alpha]_D$ for the lævulose of invert sugar = 95·74. These differences are ascribed by the authors to a peculiar modifying influence of the strong acids on lævulose. Dextrose, when added to a solution of lævulose in quantity equal to the lævulose present, does not modify the specific rotatory power of the lævulose.

Pure lævulose with 10 p.c. HCl gave, at 12°C., $[\alpha]_D = -94·66$. After heating for half-an-hour to 68°C., with 5 p.c. HCl, gave $[\alpha]_D = -96·78$. H_2SO_4 used in a similar manner gave $[\alpha]_D = -99·78$. This action of strong acids is exerted instantly, and even at ordinary temperatures. HCl added in the cold to a lævulose solution gave $[\alpha]_D = -96·50$. Oxalic acid behaves similarly on heating, whilst acetic and formic acids have no action.

Thus under conditions where pure lævulose gave $[\alpha]_D = -94·66$, the lævulose of invert sugar inverted by 5 p.c. HA, 30 mins. at 100°C. gave $[\alpha]_D = -94·48$; 10 p.c. HA, 60 mins. at 100°C. gave $[\alpha]_D = -94·00$; 5 p.c. formic acid, 30 mins. at 100°C. gave $[\alpha]_D = -94·80$. On the addition of HCl to such solutions, the readings were increased as before. Hence it would appear that the lævulose of invert sugar made by the ordinary process of inversion with acid is not identical with pure crystallised lævulose, but is a modification of it. The optical activity of dextrose is not influenced under any of the above conditions.

Ost (B. 24, 1636), who to some extent confirms the observations of Hönig and Schubert, and of Jungfleisch and Grimbert, finds the following formula for the specific rotatory power of lævulose at 20°C.:

$$[\alpha]_D^{20°} = -(91·90 + 0·111p),$$

where p is the weight in grms. of lævulose in 100 grms. of the solution.

22. *Specific Rotatory Power of Invert Sugar* $C_{12}H_{24}O_{12}$. When cane sugar is acted upon by acids, or by invertase, it undergoes hydration and thus becomes inverted. The sugars derived from it are dextrose and lævulose in equal proportions.

Dubrunfaut (C. R. 42, 901) observed that the rotatory power of invert sugar rapidly decreases with an increase of temperature. He found for a solution of invert sugar (concentration not given): $[\alpha]_j = -26·65$, at 14°C.; at 52°C., −13·33; at 90°, 0·0.

Tuchschmid (J. pr. 2, 235) found that a solution of invert sugar, $c = 17·21$, has at 0°C. a specific rotatory power $[\alpha]_D = -27·9$, and that at 87·2°C. this rotation becomes 0, according to the formula $[\alpha]_D^t = -(27·9 - 0·32t)$.

Gubbe (B. 18, 2207) states that the specific rotatory power of a solution of invert sugar depends not only upon concentration and temperature, but also upon the nature and proportion of acid used for the inversion. For instance, in the case of sulphuric and hydrochloric acids the specific rotation increases with the proportion of acid, according to the formula:

$$[\alpha]_{\mathrm{D}}^{20^\circ} = -(19{\cdot}983 + {\cdot}16979x\mathrm{H_2SO_4});$$

or $-19{\cdot}995 + {\cdot}3261x\mathrm{HCl}$); whereas oxalic acid exerts no influence.

For influence of concentration, Gubbe gives, for solutions at 20°C., containing less than 35 p.c. sugar:

$$[\alpha]_{\mathrm{D}}^{20^\circ} = -23{\cdot}305 + 0{\cdot}01612q \times {\cdot}0002239q^2;$$

and for changes of temperature from 0° to 30°C.:

$$[\alpha]_{\mathrm{D}}^{t} = -23{\cdot}305 + {\cdot}30406(t-20) + {\cdot}001654(t-20)^2.$$

These observations have to a large extent been confirmed by Jungfleisch and Grimbert in their observations on lævulose.

Ost (B. 24, 1636) also confirms Gubbe's results for dilute solutions of oxalic acid, and finds that a 0·1 p.c. solution of oxalic acid at 50°–53°C. has no influence on the specific rotatory power of invert sugar even after several hours; he finds, however, contrary to the statement of Jungfleisch and Grimbert, that a 5 p.c. solution of acetic acid lowers the rotatory power of invert sugar, even at the ordinary temperature, from $[\alpha]_{\mathrm{D}}^{20^\circ} = -20{\cdot}3$ to $[\alpha]_{\mathrm{D}}^{20^\circ} = -19{\cdot}77$.

J. O'Sullivan (C. J. 61, 408) states that invert sugar obtained from cane sugar by means of invertase has a specific rotatory power $[\alpha]_{\mathrm{j}}^{15\,5^\circ} = -24{\cdot}5$ $c = 10$, and that it yields a dextrose possessing a specific rotatory power $[\alpha]_{\mathrm{j}} = 57^\circ$, $c = 10$.

Whence O'Sullivan deduces the apparent specific rotatory power of lævulose calculated from these numbers to be $-24{\cdot}5^\circ \times 2 - 57^\circ = -106$ for $[\alpha]_{\mathrm{j}}^{15{\cdot}5^\circ}$.

23. *Specific Rotatory Power of Maltose* $\mathrm{C_{12}H_{22}O_{11}}$. The specific rotatory power of maltose has been determined by several observers.

O'Sullivan, who first critically examined this sugar, finds the following values (C. J. 29, 480 and 45, 1): $[\alpha]_{\mathrm{D}} = 139^\circ$; $[\alpha]_{\mathrm{j}} = 154^\circ$; for $c = 10$.

Brown and Heron (C. J. 35, 596) find 153·1°.

Other values have been found as follows:—

Musculus Von Mering	$[\alpha]_{\mathrm{j}} = 149{\cdot}0$ (Z. P. C. 2, 403);
Yoshida . . .	$[\alpha]_{\mathrm{j}} = 150{\cdot}25$ (C. N. 43, 29);
Sandwik . . .	$[\alpha]_{\mathrm{j}} = 150$ (*Z.* P. C. 5, 427);
Schulze . . .	$[\alpha]_{\mathrm{j}} = 149{\cdot}5$ (B. 7, 1847);
Herzfeld . . .	$[\alpha]_{\mathrm{D}} = 140{\cdot}6$ (B. C. 1883, 127).

Meissl (*J. pr.* [2] 25, 114), on making experiments with various preparations of maltose, finds that its specific rotatory power varies inversely with the temperature and concentration. As the mean of several experiments he gives the following equation for the specific rotatory power of maltose: $[\alpha]_{\mathrm{D}} = 140{\cdot}375 - 0{\cdot}01837\,\mathrm{P} - 0{\cdot}095t$, where t = temperature, P = percentage of maltose in the aqueous solution.

For all practical purposes the numbers given by O'Sullivan as above may be taken as correct.

24. *Specific Rotatory Power of Lactose* $\mathrm{C_{12}H_{22}O_{11} + H_2O}$. Previous to the investigations of Schmoeger it was stated that the specific rotatory power of lactose varied according to concentration, and accordingly we find the following formula by Hesse (A. 176, 100) for calculating the rotatory power:

$$[\alpha]_{\mathrm{D}} = +54{\cdot}54c - {\cdot}5575c + {\cdot}05475c^2 - {\cdot}001774c^3.$$

The following values have been found for lactose by various observers:

Erdman .	$[\alpha]_{\mathrm{D}} = +51{\cdot}5$;
Poggiale .	$[\alpha]_{\mathrm{D}} = +54{\cdot}2$;
Biot . . .	$[\alpha]_{\mathrm{j}} = +60{\cdot}23$ (C. R. 42, 439);
Berthelot .	$[\alpha]_{\mathrm{j}} = +59{\cdot}3$ (Wurtz, Dict. de Chem.);
Hoppe-Seyler	$[\alpha]_{\mathrm{j}} = +58{\cdot}2$ (Handbuch Physiol. Chem. Analyse).

Schmoeger (B. 13, 1922), who in 1882 very carefully investigated the optical properties of lactose, came to the conclusion that the specific rotatory power is the same for all concentrations from 2 grms. up to 36 grms. per 100 c.c., but that temperature exerts an appreciable influence on the rotatory power; thus at 10°C. $[\alpha]_{\mathrm{D}} = 53{\cdot}5$, at 35°C $[\alpha]_{\mathrm{D}} = 51{\cdot}48$. From his experiments Schmoeger came to the conclusion that at 20°C. lactose possesses a specific rotatory power for ray D of $+52{\cdot}5^\circ$, and that the value of $[\alpha]_{\mathrm{D}}$ varies inversely about ·075° for every 1°C. In the present state of our knowledge $[\alpha]_{\mathrm{D}} = 52{\cdot}5^\circ$ may be taken as the most correct number for lactose. Pellet and Biard find (Bl. [1] 5, 171) $[\alpha]_{\mathrm{j}} = +58{\cdot}94$.

25. *Specific Rotatory Power of Dextrin* $\mathrm{C_{12}H_{20}O_{10}}$. Continental chemists following Musculus state that the different dextrins have a varying action on polarised light, and are all capable in a different degree of reducing cupric oxide. English chemists, on the other hand, contend that the dextrins have no cupric-reducing power, and that all possess the same specific rotatory power, viz. $[\alpha]_{\mathrm{j}} = 222^\circ$, $[\alpha]_{\mathrm{D}} = 200{\cdot}4$ – for $c = 10$; see O'Sullivan (C. J. 30, 125; 45, 1), Brown and Heron (C. J. 35, 596).

26. *Specific Rotatory Power of Malto-dextrins.* Brown and Morris (C. J. 47, 527; 55, 449) have isolated two bodies from starch, one by the action of diastase, the formula of which is given as $\genfrac{}{}{0pt}{}{\mathrm{C_{12}H_{22}O_{11}}}{(\mathrm{C_{12}H_{20}O_{10}})_2}$, $[\alpha]_{\mathrm{j}\,3{\cdot}86} = 193{\cdot}11$, $c = 10$; the other by the action of dilute acid in the cold on starch granules—

$$\genfrac{}{}{0pt}{}{\mathrm{C_{12}H_{22}O_{11}}}{(\mathrm{C_{12}H_{20}O_{10}})_6},\ [\alpha]_{\mathrm{j}\,3{\cdot}86} = 206{\cdot}11.$$

27. *Specific Rotatory Power of Raffinose.* Raffinose $\mathrm{C_{18}H_{32}O_{16} + 5H_2O}$ has been found to occur ready formed in eucalyptus manna, cotton seed, beetroot, and barley.

Loiseau (C. R. 82, 1058) in 1876 obtained raffinose in a crystalline form from beet sugar in the course of an investigation on the extraction of sugar from molasses with sucrate of lime. He ascribed the formula $\mathrm{C_9H_{16}O_8 + 2\frac{1}{2}H_2O}$ to it, and found that for cane sugar polarising 100 divisions on the saccharimeter raffinose polarised 159.

Ritthausen in 1884 (J. pr. [2] 29, 351) separated this body from cotton seed, and gave to it the formula $\mathrm{C_{12}H_{22}O_{11},3H_2O}$, with a specific rotatory power $[\alpha]_{\mathrm{j}} = 117{\cdot}4$, which, after inversion with acid, diminished to $[\alpha]_{\mathrm{j}} = 61{\cdot}8$.

Tollens, in 1885 (B. 18, 26), separated the same body from beet-sugar molasses resulting from the strontia process, and for which he found $[\alpha]_{\mathrm{D}} = 102{\cdot}5^\circ - 103{\cdot}0^\circ$, and after inversion $[\alpha]_{\mathrm{D}} = 45^\circ$.

Rischbiet and Tollens (B. 18, 2611) found the same substance in eucalyptus manna in

TABLE VI. *Specific Rotatory Powers of Carbohydrates.*

—	$[\alpha]_D$	$[\alpha]_j$	$[\alpha]_{D3\cdot86}$	$[\alpha]_{j3\cdot86}$	Readings for 1 grm. per 100 c.c. in 200 mm. tube in Scale of	
					Laurent's polarimeter	Soleil-Ventzke-Scheibler saccharimeter
Cane sugar	+ 66·5	+ 73·8	+ 66·5	+ 73·8	+ 1·330	+ 3·84
Maltose	+ 139·0	+ 154	+ 135·4	+ 150	+ 2·708	+ 7·81
Lactose at 20°C. . . .	+ 52·5	+ 58·9	—	—	—	—
Dextrose	+ 52·7	+ 57·0	+ 52·7	+ 57·0	+ 1·054	+ 2·97
Laevulose —						
From inulin at 20°C. .	− 91·0	—	—	—	—	—
From invert sugar at 20°C. .	− 95·5	− 104·8	—	—	—	—
Invert sugar at 15° C. . .	− 21·5	—	—	—	—	—
Raffinose	+ 104·4	+ 135·3	—	—	—	—
Dextrin	+ 200·4	+ 222·0	+ 195·0	+ 216	+ 3·900	+ 11·25
Maltodextrin I. . . .	—	—	—	+ 193·1	—	+ 10·05
Maltodextrin II. . . .	—	—	—	+ 206·1	—	+ 10·74

TABLE VII.

—	Solvent	Concentration c =	$[\alpha]_D$
Quinine hydrate $C_{20}H_{24}N_2O_2 + 3H_2O$	Alcohol, 97 p.c. by vol.	1 to 10	$-(145\cdot2-0\cdot657c)$
Hydrochloride $C_{20}H_{24}N_2O_2.HCl + 2H_2O$.	Water	1 to 3	$-(144\cdot98-3\cdot15c)$
Same, 1 mol. of salt	2 mols. HCl + H_2O to 100 c.c.	1 to 7	$-(229\cdot46-2\cdot21c)$
Sulphate (neutral) $2(C_{20}H_{24}N_2O_2).H_2SO_4 + 8H_2O$	Alcohol, 80 p.c. by vol.	2	−162·95
Same, 1 mol. anhydrous sulphate .	4 mols. HCl + H_2O to 100 c.c.	2	−239·2
Sulphate (mono acid) $C_{20}H_{24}N_2O_2.H_2SO_4 + 7H_2O$	Water	1 to 6	$-(164\cdot85-0\cdot31c)$
Disulphate (diacid) $C_{20}H_{24}N_2O_2.2H_2SO_4 + 4H_2O$	Water	2 to 10	$-(155\cdot69-1\cdot14c)$
Cinchonidine $C_{20}H_{24}N_2O$ . .	Alcohol, 97 p.c. by vol.	1 to 5	$-(107\cdot48-0\cdot297c)$
Hydrochloride $C_{20}H_{24}N_2O.HCl + H_2O$.	Water	1 to 3	$-(105\cdot34-0\cdot76c)$
Same, 1 mol. salt	2 mols. HCl + H_2O to 100 c.c.	1 to 10	$-(154\cdot07-1\cdot39c)$
Sulphate (neutral) $2(C_{20}H_{24}N_2O).H_2SO_4 + 6H_2O$	Water	1·06	−106·77
Sulphate (mono-acid) $C_{20}H_{24}N_2O.H_2SO_4 + 5H_2O$	Water	2·0	−110·5
Disulphate (di-acid) $C_{20}H_{24}N_2O.2H_2SO_4 + 2H_2O$	Water	1 to 7	$-(105\cdot96-1\cdot0267c$ $+0\cdot0376c^2$ $-0\cdot00104c^3)$
Quinidine hydrate $C_{20}H_{24}N_2O_2 + 2\frac{1}{2}H_2O$	Alcohol, 97 p.c. by vol.	1 to 3	$+(236\cdot77-3\cdot01c)$
Hydrochloride $C_{20}H_{24}N_2O_2.HCl + H_2O$.	Water	1 to 2	$+(205\cdot83-4\cdot93c)$
Same, 1 mol. salt	2 mols. HCl + water to 100 c.c.	1 to 5	$+(292\cdot56-3\cdot09c)$
Diquinidine sulphate $2(C_{20}H_{24}N_2O_2).H_2SO_4 + 2H_2O$	Water	1	+179·54
Sulphate $C_{20}H_{24}N_2O_2.H_2SO_4 + 4H_2O$.	Water	2 to 8	$+(212\cdot0-0\cdot8c)$
Cinchonine $C_{20}H_{24}N_2O$ . . .	Alcohol 97 p.c. by vol.	0·5 to 1	+226·13
Hydrochloride $C_{20}H_{24}N_2O.HCl + 2H_2O$.	Water	0·5 to 3	$+(165\cdot5-2\cdot425c)$
Same, 1 mol. salt	2 mols. HCl + water to 100 c.c.	1 to 7	$+(214\cdot0-1\cdot72c)$
Dicinchonine sulphate $2(C_{20}H_{24}N_2O).H_2SO_4 + 2H_2O$	Water	1 to 2	$+(170\cdot3-0\cdot855c)$

1886, and proved that it was identical with the body extracted from molasses and cotton seed by other observers.

Scheibler (B. 18, 1779) found for the same body $[\alpha]_D = 103\cdot9$ and $[\alpha]_j = 114\cdot6$; on inversion $[\alpha]_D = 52\cdot3$, and the formula $C_{18}H_{32}O_{16}.5H_2O$.

Pellet and Biard in 1886 confirmed Loiseau's experiments (C. C. 47, 878).

C. O'Sullivan (C. J. 49, 70) in the same year found raffinose in barley, and the specific rotatory power for anhydrous raffinose to be $[\alpha]_j = 135\cdot3$, and on inversion $[\alpha]_j = 43\cdot5$. He gave to it the formula $C_{18}H_{32}O_{16}.5H_2O$.

Beythien and Tollens, who have more recently studied the properties of raffinose (Ann. [2] 55, 195), agree with Scheibler and O'Sullivan as to the formula $C_{18}H_{32}O_{16}$, and find $[\alpha]_D = 104\cdot4$, a number which is now generally accepted as the correct one.

In Table VI. the specific rotatory powers of the various carbohydrates are given for concentration $c = 10$.

28. *Specific Rotatory Power of the Cinchona Alkaloids.* The rotation constants which have been determined with the greatest accuracy by Hesse (Ann. 176, 203, and 182, 128) are those of quinine, cinchonidine, conchinine (quinidine), and cinchonine. In each of these four alkaloids the specific rotation varies considerably with the nature of the solvent, and increases, moreover, with the increase of concentration. Hesse has investigated the rotation of solutions containing, according to their respective solvent powers, from 1 to 10 grms. of substance in a 100 c.c. of solution, and has found that within these limits the variations are represented by the formulæ $[\alpha] = A - Bc$. As solvent, alcohol of 97 p.c. by volume was employed for the pure alkaloids, and for their salts either water, dilute hydrochloric, or sulphuric acid of known strength, the latter being added in such quantity that the solutions contained for one molecule alkaloid not more than 3 molecules HCl or H_2SO_4. This was the proportion of acid used also in the solutions of the free alkaloids. In calculating the number of c.c. of standard acid to be added to a given weight of alkaloid, Hesse took 316 for the molecular weight of all four bases, being the mean of 308 ($C_{20}H_{24}N_2O_4$, cinchonine and cinchonidine), and 324 ($C_{20}H_{24}N_2O_2$, quinine and quinidine). The error arising from the slight difference from the true molecular weight is trifling.

As the rotatory power of solutions containing alkaloids decreases more or less with a rise of temperature, the solutions must be kept at a constant temperature. Hesse took 15°C. as a standard.

Table VII. shows the constants obtained by Hesse with preparations of the highest possible degree of purity.

As in previous cases c stands for the number of grms. of active substance in 100 c.c. of solution.

29. *Specific Rotatory Power of Vegetable Oils.* It has generally been taken for granted that all vegetable oils (with the exception of castor and resin oils) have no action on polarised light, but recent observations by Bishop (J. Ph. [5] 16, 300) and Peter (Bl. 48, 483) tend to show that many oils cause a most decided rotation of the polarised ray, as is seen in the accompanying table:—

Table VIII.

—	Laurent's polarimeter	Saccharimetric scale
Olive oil, refined .	+0·16°	+0·7 divs.
„ „ commercial	+0·28°	+1·3 „
Sesame oil, refined .	+1·08°	+5·0 „
„ „ commercial	+1·95°	+9·0 „
Castor oil . .	+8·8°	+40·7 „
Croton oil . .	+9·25°	+42·6 „
Colza oil . . .	−0·26°	− 1·2 „
Sweet almond oil .	—	− 0·7 „
Linseed oil . .	—	− 0·3 „

These experiments want further corroboration by observations made on several samples of pure oils from widely different districts before a methodical table can be constructed for the purpose of detecting adulteration, or of ascertaining the relative purity of commercial samples. There can be no doubt, however, that such a series of observations on the action of the different oils on polarised light would be of extreme value, and would in time form a useful adjunct to the present methods of analysis.

Practical Applications.

30. *Determination of cane sugar, other optically-active bodies being absent.*

The determination of the percentage of cane sugar in aqueous solutions is founded upon the following propositions established by Biot.

1. The amount of deviation of the plane of polarisation is proportional to the length of the liquid column.

2. The amount of deviation is proportional to the concentration—*i.e.* number of grms. of sugar in 100 c.c. of solution. Therefore, by determining once and for all the amount of deviation produced by a given solution of pure cane sugar of known concentration c in a tube of a given length, l, the number of grms. of sugar per 100 c.c. in any solution of unknown strength can easily be calculated, and hence the percentage of sugar on weight taken according to the following formula:

$$c = \frac{100\alpha}{l \times [\alpha]}.$$

Where an instrument with angular graduation is employed, the most convenient proportion of sugar to use is 15 grms. per 100 c.c., and substituting the value of $[\alpha]_D = 66\cdot5$ in the above equation:

$c = \dfrac{100\alpha}{l \times 66\cdot5} = 1\cdot504\,\dfrac{\alpha}{l}$, in which α is the angle of rotation observed with the sodium light and l the length of tube employed. If $l = 200$ mm. then $c = 0\cdot75\alpha$. A solution of 15 grms. per 100 c.c. of pure dry cane sugar gives an angle of 20° exactly, which multiplied by 5 gives 100. If, therefore, 15 grms. of a sample of commercial sugar are weighed out, and made into a 100 c.c. solution and polarised in a 200 mm. tube, the real sugar percentage may be obtained by simply multiplying by 5.

Should, however, any other weight P be taken per 100 c.c. the percentage may be calculated from the proportion $P : 0{\cdot}75a :: 100 : x$,

$$\text{whence } x = \frac{75a}{P}.$$

In the case of a Soleil-Ventzke-Scheibler or Schmidt and Haensch saccharimeter, in order to estimate the percentage of cane sugar in a commercial sample, all that is necessary to do is to weigh out 26·048 grms. of the sample, dissolve in water, make up to 100 c.c. at 15·5°C., and observe the deviation produced by it in a 200 mm. tube; the number observed expresses directly the percentage of pure cane sugar in the sample.

Where a Soleil-Duboscq instrument is employed, 16·35 grms. of the sample are taken, made into a 100 c.c. solution, and polarised; the reading observed giving directly the percentage of sugar.

In the case of loaf and good crystal sugars the solution will be sufficiently clear and colourless to be capable of being polarised at once; in actual practice, however, the analysis of such samples is but rarely required, and in dealing with all other qualities of sugars it will be necessary to remove the colouring matter to a greater or less extent before proceeding to polarise them.

Where the solution exhibits only a slight turbidity or opalescence this may be got rid of by the addition of a little alumina cream to the solution in the flask before making it up with water to the containing mark. Of course, after it is made up it must be well shaken and filtered bright before it can be polarised. For dark solutions clarification is usually effected with basic lead acetate. The normal weight of sugar, having been weighed out, is dissolved in about 50 c.c. of water, using heat if necessary, then cooled to 15·5°C. and transferred to a 100 c.c. flask provided with a long neck, on which is a second mark indicating 110 c.c. The liquid in the flask is made up to the first mark, 100 c.c., with distilled water at 15·5°C., and as much basic lead acetate added as will just precipitate the colouring matter. This usually amounts to from 3 c.c. to 5 c.c. The liquid is then made up with distilled water to the second mark, about 3 grms. of freshly-burnt finely-powdered dry animal charcoal is then added, the whole shaken up well, and, after a few minutes, filtered. The first 5 c.c. or so of the filtrate must be rejected. If the filtrate does not then come through bright it must be poured back on the filter until it does. It will then be suitable for polarising. In this case it will be found convenient to use a 220 mm. tube instead of a 200 mm. —or, if a 200 mm. tube be used, the reading must be multiplied by $\frac{11}{10}$ to correct for dilution from 100 c.c. to 110 c.c.

In the case of molasses and syrups it is advisable to use half the normal weight, and make up as usual to 100 c.c., clarification being effected with 7–8 c.c. basic lead acetate and animal charcoal; after filtration, the optical activity is observed in a 220 mm. tube, and the result multiplied by 2; or, if observed in a 200 mm. tube, multiplied by $\frac{11}{10} \times 2 = \frac{22}{10}$.

Where acetate of lead is used, Casamajor (C. N. 25, 306) recommends the addition of soluble salts capable of giving dense precipitates with the lead—such as sodium sulphate or phosphate. The soluble salt is added by throwing a pinch of it on the sugar, and dissolving by water afterwards. The addition of the salts mentioned does not affect the polarisation.

Solutions of raw sugars after treatment with lead acetate frequently take a long time to filter, and when large numbers of samples have to be polarised in the course of the day much inconvenience sometimes results. In order to obviate this a solution of bleaching powder has been employed by the writer with excellent results.

A quarter of a pound of dry bleaching powder is rubbed up in a mortar with half a pint of distilled water until the whole is reduced to a thin mud of uniform consistency, then thrown on a filter. The filtrate is preserved in a tightly-fitting stoppered bottle in a cold, dark place. To 100 c.c. of the sugar solution made up in the way already described are added about 5 c.c. of the bleaching solution, and let lie a minute or two, until the solution is completely decolourised. The mixture of the bleaching solution with the liquid in the flask may be accelerated by twisting the neck of the flask between the hands, so as to impart a rotary motion to it. A few c.c. of sulphurous acid, sp.gr. 1,020, are next added, the liquid made up with distilled water to the second mark, well shaken up, and filtered if necessary. By this process, unless the sugar solution is cloudy or turbid before the addition of the bleaching solution, no filtration is required, so that much time is saved; and from several experiments the writer has assured himself that the bleaching solution has no action on the specific rotation of the optically-active bodies present.

31. *Determination of cane sugar, other optically-active substances being present.* When only cane sugar is present it can, as we have just seen, be determined at once by direct polarisation, but when dealing with the lower grade beet sugars, and East and West Indian raw sugars, molasses, syrups, &c., the cane sugar is generally accompanied by greater or less quantities of invert sugar, the effect of which is to reduce the polarisation, so that the correct percentage of cane sugar cannot be directly determined, and recourse must be had in such cases to the so-called inversion process of Clerget, which was introduced by him in 1845, and is known as the double polarisation process—that is to say, polarisation of the sample before and after inversion. It has been universally adopted as the most accurate, as well as the most convenient, method to use for the estimation of cane sugar in commercial samples.

According to Clerget's experiments, a solution of pure cane sugar which indicates a rotation of 100 divisions to the right on the saccharimetric scale will, after inversion by acid and at a temperature of 0°C., show a rotation of 44 divisions to the left on the same scale, the total change of rotation being 144 divisions. It has been found, moreover, that this relation varies considerably with the temperature at which the reading is taken, and it was found that alteration of rotation was equal to 0·5 division for a rise of 1°C.

Thus, at 0°C. the total change of rotation, which was equal to 144 divisions, would at 1°C. become $144 - 0{\cdot}5 = 143{\cdot}5$; at 2°, $144 - 1 = 143$; and generally at a temperature t° the amount of change would be represented by $144 - \frac{1}{2}t$. If then S represent the sum or difference of the saccharimetric reading before and after inversion, t° the temperature of the inverted solution at time of observation, and R the percentage of cane sugar sought, then $(144 - \frac{1}{2}t) : 100 :: S : R$, whence $R = \frac{100S}{144 - \frac{1}{2}t}$.

This method, since first introduced by Clerget, has been submitted to most careful investigation by many other chemists with a view of determining the accuracy of Clerget's results, as well as the best method of procedure.

Since Clerget's time the Soleil saccharimeter has gradually been replaced by the Soleil-Ventzke-Scheibler, and Schmidt and Haensch's half-shadow saccharimeters, and for either of these instruments, of the various methods proposed from time to time for the determination of cane sugar by double polarisation, the modification of Clerget's process recommended by Herzfeld is the one now universally adopted. This is as follows:—26·048 grms. of the sugar to be examined are dissolved in water and made up to 100 c.c., decolourised if necessary, filtered, &c., and polarised. 50 c.c. of this solution are then taken in a 100 c.c. flask, 5 c.c. of 38 p.c. hydrochloric acid added, and about 20 c.c. of water. The flask is then well shaken and plunged into water, heated to a temperature of 70°C. as soon as the temperature of the sugar solution has risen to 68–70°C., which it should do in five minutes, it is kept in the water-bath at this temperature for five minutes longer, then taken out, cooled down quickly to the normal temperature, diluted with water to 100 c.c., polarised at 20°C., and the reading multiplied by two.

It is hardly necessary to remark that the sugar solution, previous to inversion, should be polarised at the same temperature, otherwise a slight error may be introduced in calculating out the results, owing to the invert sugar which may be present in the original sample.

According to Herzfeld, a solution of pure cane sugar, containing 26·048 grms. of sugar per 100 c.c., should by this method show a change of rotation on a Soleil-Ventzke-Scheibler saccharimeter of 132·6 divisions at 20°C., so that for this temperature Clerget's formula becomes $R = \frac{100S}{132{\cdot}6}$; this at 0°C. becomes $\frac{100S}{142{\cdot}6}$, a number differing slightly from that first determined by Clerget. Where a temperature other than 20° is employed, the results may therefore be calculated by the formula

$$R = \frac{100S}{142{\cdot}6 - \frac{t^\circ}{2}}.$$

Where raffinose is suspected to be present, as in those sugars which are recovered from molasses, especially such as result from the osmose or strontia process, the formula for this substance must be applied instead of Clerget's. The one recommended in the official instructions published in connection with the German Sugar Duties Act of July 9, 1887, is perhaps as good a one as any, and was proposed by Dammuller (Zeit. f. Zuckerind. 1888, 742).

To calculate the result the following formulæ are used:

$$S = \frac{0{\cdot}5188P - P'}{0{\cdot}845}, \quad R = \frac{P - S}{1{\cdot}85};$$

where S = cane sugar p.c., R = raffinose p.c., P = polarimetric reading for the whole normal weight before inversion, P′ = polarimetric reading for the whole normal weight after inversion.

Instead of carrying out the inversion of cane sugar by means of acid, O'Sullivan and Tompson's invertase process (C. J. 59, 46) may be employed, being advantageous in such solutions as those obtained from malt and other natural sources, where the use of acid is inadmissible or would lead to inaccuracy by reason of its action on other bodies which might be present in such solutions.

The method of procedure is as follows:—The solution containing the cane sugar must be approximately neutral (certainly not alkaline), and if the presence of any enzyme is suspected the temperature should be momentarily raised to 80°C. to destroy it. The optical activity at 15·5°C. and the cupric reducing power of the solution are determined, and then 50 c.c. of it are poured into a beaker and raised to a temperature of 55°C. in a constant temperature bath. Some ordinary brewer's yeast, pressed in a towel, is now taken. The weight of the pressed yeast should be about one-tenth of the total amount of sugar to be inverted. It is thrown into the hot solution, and the whole gently stirred until the mixture is complete. The solution is left for four hours in the water-bath. At the end of this time it is cooled to 15·5°, a little freshly precipitated aluminium hydrate added to facilitate filtration (this is not always necessary), and the whole made up to 100 c.c. A portion of this solution is filtered, and the optical activity observed. The solution is then left in the cold until the next day, when another observation is taken in order to prove that inversion is complete. The cupric reducing power may also be estimated, if desired. The results are calculated as follows:—

(*a*) *From the optical activity* the cane sugar may be calculated as follows:—

$$P = \frac{\alpha - 2\alpha'}{m}.$$

α = the number of divisions indicated by the polarimeter scale for 200 mm. of the original solution.

α' = the same factor in the inverted solution.

m = the number of divisions of the polarimeter scale which 200 mm. of a solution containing 1 grm. of cane sugar per 100 c.c. alters on being inverted. In the case of the Soleil-Ventzke-Scheibler saccharimeter 1 grm. of cane sugar in 100 c.c. indicates + 3·84 divisions, whereas after inversion it gives − 1·34 divisions. Therefore, where this instrument is used $m = 5{\cdot}18$.

P = the weight of cane sugar present in 100 c.c. of the original solution.

(*b*) *From the cupric reducing power*

$$P = 0\cdot4308\left(\frac{2G'k'}{w'} - \frac{Gk}{w}\right)$$

Where G = the weight of 100 c.c. of the original solution.

G′ = the same factor for the inverted solution. Allowance must, of course, be made here for dilution and for the 5 p.c. increase of the inverted sugar, but the latter number is so small that it need not be calculated accurately.

w = the weight of the original solution used for the estimation.

w' = the same factor for the inverted solution.

k = the weight of the cupric oxide reduced by w.

k' = the same factor for w'.

P = the weight of cane sugar present in 100 c.c. of the original solution.

It is needless to remark that the values of P in both cases should be identical within the limits of error of manipulation.[1]

Where preferred, a solution of invertase may be used instead of yeast; this is prepared, according to O'Sullivan and Tompson, as follows (C. J. 57, 880):

Yeast is allowed to liquefy for at least a month in a fairly warm room, care being taken not to stir it or otherwise disturb it during this period; the surface liquor is then removed, and the lower layer thrown on to a quick filter. To this yeast liquor is then added a sufficient quantity of alcohol so that the whole bulk of the liquid contains about 10–12 p.c. absolute alcohol. The mixture is allowed to stand a few days, and then the clear solution is filtered off. This solution is kept in a stoppered bottle, and retains its inverting power indefinitely.

32. *Analysis of raw sugars.* Sugars, whether raw or refined, which are fit for direct consumption are generally valued from their appearance, colour, size of grain, brightness, &c., rather than according to the percentage of sugar present; but where sugars are bought for purposes of refining it becomes most essential for the refiner not only to know how much cane sugar the sample actually contains, but also the amount of cane sugar which he can obtain in the process of refining, and which is known as the available amount of crystallisable sugar. For it is a well-known fact that several samples which may show the same percentage of sugar by polarisation will not all yield equal amounts of crystallisable sugar on refining; and these differences are attributed to the presence in greater or less quantities of the salts of mineral and organic acids, as well as to the presence of invert sugar, and organic bodies other than sugar, all of which exercise to a certain extent an injurious effect upon the crystallisation of the cane sugar.

A study of these bodies and their effects has given rise to a method of valuing raw sugars, which has been adopted in France and Germany as well as in this country, and is known as the 'rendement,' or the net amount of crystallisable sugar obtainable from a given sample of raw sugar.

This method assumes that for every 1 p.c. of ash contained in the raw sugar 5 p.c. of cane sugar is prevented from crystallising, and that for every 1 p.c. of invert sugar present an equal proportion of cane sugar is retained in the molasses. Hence the rule: from the amount of cane sugar found by polarisation deduct five times the weight of ash plus the weight of the invert sugar which may be present. The remainder is taken as the refining value or 'rendement' of the sample. Thus a sugar showing on analysis

Cane sugar	95 p.c.
Invert sugar	2 ,,
Ash	1 ,,

would, according to the above method, give $95 - (1 \times 5 + 2) = 88$ p.c. available crystallisable sugar.

On the Continent a beet sugar giving in this way a 'rendement' of 88 is fixed on as a standard of value, and all sugars are sold at so much a degree more or less than this standard.

In the complete analysis of sugars for commercial purposes the following determinations are usually made:

1. Cane sugar, or crystallisable sugar.
2. Uncrystallisable sugar. This includes invert sugar, as well as any other substances which reduce Fehling's solution, but which are all classed as invert sugar.
3. Mineral matters or ash.
4. Water.
5. Organic matters, not sugar, or unknown organic matters.
6. Insoluble matters, such as sand, clay, portions of fibre, &c., if present.

1, 2, 3, 4 and 6 are generally determined direct, and after calculating the percentage of each the difference between the sum of these and 100 is put down as organic matters not sugar, and includes certain alkaloids, nitrogenous bodies, various organic acids, cellulose, gum, fatty bodies, colouring matters, &c.

Much care should be exercised in the collection of samples for analysis, more especially of the low-class sugars, which contain much moisture and appreciable quantities of insoluble matters. Of these the analyst should receive at least two pounds weight of each lot to be tested, and representing as closely as possible an average sample of the original. All lumps should be well broken up, the whole thoroughly mixed, and, where practicable, run once through a coarse sieve.

The average sample thus obtained is preserved in a wide-mouthed bottle, having a well-fitting stopper.

Determination of cane sugar. This is determined by double polarisation, as already described.

Determination of invert sugar or glucose. This is best accomplished gravimetrically by means of Fehling's solution. 10 grms. of the sample of sugar are carefully weighed out, made into a 100 c.c. solution, and filtered if necessary. 40 c.c. of Fehling's solution are taken in a beaker of 150 c.c. capacity with about 60 c.c. of boiling and well-boiled distilled water and placed in another beaker of boiling water, which is kept boiling on a sand-bath over a Bunsen. At the end of five or six minutes, when the copper solution has acquired, as nearly as possible, the temperature of the surrounding water, exactly 10 c.c. of the sugar solution, measured by means of an accurately graduated pipette or burette, are run into the copper solution, and the heating continued for twelve minutes. Where greater accuracy is required, the quantity of sugar solution is weighed in a small tared beaker, and the volume found by dividing the weight of the solution by its specific gravity. After heating for twelve minutes, the cuprous oxide precipitated by the reducible sugars present is filtered quickly, either through a paper or an asbestos filter, thoroughly well washed with boiling well-boiled water, dried, ignited for fifteen minutes, and weighed. The weight of cupric oxide thus obtained divided by 2·205, or multiplied by its reciprocal ·4535, gives the amount of invert sugar in the quantity taken, from whence may be calculated the percentage of invert sugar present.

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[1] It is not necessary to [illegible] result is sufficient. The op[illegible] more convenient, and generally the more accurate, of the two, except where much invert sugar is present in the sample before inversion (see section [illegible]

Determination of ash. (*a*) *Total ash.* About 5 grms. of the sugar are weighed out into a platinum dish of about 100 c.c. capacity, and well moistened with about twenty drops of sulphuric acid (sp.gr. 1·600), and a little ether poured over the contents of the dish, which are then gently ignited over the Bunsen flame. By this means a porous carbonised mass is obtained, which is kept at a dull red heat in a muffle until all the carbonaceous matter is burned away, and nothing but a white or greyish-white ash is left. When a muffle is not available, ignition over a Bunsen burner answers just as well. The dish and contents are then allowed to cool and weighed; the dish is washed clean of ash, heated gently, cooled, and again weighed, the difference between the two being the weight of the sulphated ash.

(*b*) *Soluble ash.* Where a complete analysis of a sample of sugar is required, it is, of course, necessary to know the total amount of mineral matter present, but as in some low quality sugars considerable amounts of insoluble matter —consisting of clay, sand, carbonate of lime, &c. —are present which in the process of defæcation become precipitated or filtered off and do not interfere with the crystallisation of the sugar, it becomes necessary for the refiner to know the amount of soluble mineral matter which is present, and which does exert an influence on the crystallisation. For this purpose 50 c.c. of the solution used for the determination of the invert sugar are measured into a platinum dish, about twenty drops of strong sulphuric acid added, and the whole evaporated down to complete dryness, which then becomes a charred mass. This is ignited in a muffle or over a Bunsen until all the carbonaceous matter is driven off, cooled, and weighed as before.

(*c*) *Insoluble ash.* The difference between the total and the soluble ash gives the amount of insoluble ash which may be present; or the insoluble ash may be determined directly as follows: 20 to 50 grms. of the sugar are taken in a beaker, about 100 c.c. water added, and the solution filtered. The residue is repeatedly washed with water until all the soluble matter is completely extracted, collected on the filter, dried, and ignited.

The addition of sulphuric acid converts the various salts (phosphates excepted) into sulphates, and as the sulphated ash is generally considered to weigh heavier than the ash obtained in the ordinary process of carbonisation, it is usual to deduct 10 p.c. of its weight in order to obtain a more correct result. This subtraction of one-tenth of the weight of the sulphated ash is generally assumed to answer for beet sugars, but does not apply in all cases to cane sugars, least of all to the low-class raw sugars, and where lime salts abound; and, from an extensive series of determinations of cane sugar ash, the writer has come to the conclusion that more accurate results are obtained by not subtracting one-tenth of its weight from the sulphated ash. Recently, the results of other chemists appear to confirm this view (*v.* Wiechmann, School of Mines Quarterly, 2, 1).

Where alkaline salts are largely present in the ash, as in beet sugars, it is almost impossible to completely burn away the last portions of carbonaceous or organic matter. In such cases the soluble salts are first extracted from the carbonised mass with boiling water, the carbonaceous residue collected on a filter, dried, and well ignited; this is added to the aqueous extract, which is then evaporated to dryness in a platinum dish, gently ignited, and weighed.

Determination of water. In text-books the method for determining the amount of moisture present in any given sample of sugar is somewhat as follows:

Where the sample is of fair quality containing little or no invert sugar, from 5 to 10 grms. are weighed out into a flat dish, dried at 100°C., and weighed until constant; in this case sufficiently accurate results for all purposes are obtained.

If the water is to be determined in a moist sugar or in a syrup, about 2 grms. only of the sample are taken, mixed up intimately with about 20 grms. of pure dry sand, and dried in an oven or air-bath, in which the heat is gradually carried up to between 95° and 100°C., and the drying then continued at this temperature until the weight is constant. The weight of the sand and dish, deducted from the total weight, gives the weight of the dry sugar, and hence the moisture. The above operation may to a certain extent be hastened by adding a small quantity of 70 p.c. alcohol to the mixture of sand and sugar, and drying in an oven at 70–80°C. until the alcohol is nearly driven off, then moistening thoroughly with absolute alcohol, drying at 75°C. for thirty minutes, then at the temperature of boiling water for an hour, weighing, and again drying and weighing until constant.

The cane sugar (and raffinose where present), invert sugar or glucose, ash and water having been determined are added together, and any difference between the sum of these and 100 is recorded as 'undetermined organic matters,' or 'other organic matters,' or 'unknown organic matters' (Fr., *matières indeterminées*; Ger., *organischer nichtzucker*).

Where much invert sugar is present, the lævulose is very liable to undergo decomposition upon being exposed to so high a temperature for so long a time, and hence the results will invariably be too low. In order to obviate this, the following method has been devised by the writer as being more accurate and may be applied to all classes of sugars as well as to the other carbohydrates.

From a great many determinations of the specific gravity of solutions of the ash of raw and refined sugars, obtained from widely-differing sources, the writer finds that 1 grm. of ash per 100 c.c. of water gives a sp.gr. of 1008. Therefore, if from the specific gravity of the sugar solution (10 grms. per 100 c.c.) be deducted the specific gravity due to the soluble ash (grms. of ash per 100 c.c. × 8), and the remainder be divided by 3·86, and multiplied by 10, the total amount of solids per cent., less the ash, is obtained. To the amount of total solids thus obtained is added the percentage of soluble ash, plus the percentage of insoluble ash; the sum, subtracted from 100, gives the percentage of water.

The examples given below show the method of analysis.

Analysis of jaggery sugar.

Cane sugar. 26·048 grms. were made into a 100 c.c. solution, decolourised, filtered, and polarised in 200 mm. tube at 20°C.

50 c.c. of a similar solution were taken in a 100 c.c. flask, 5 c.c. 38 p.c. HCl added, made up with water to 75 c.c., and plunged into the water-bath, the temperature of which was slightly over 70°C. The temperature of the sugar solution rose in about five minutes to 68°, at which temperature it was maintained for five minutes longer, then taken out, cooled rapidly to 20°C., decolourised, made up with water to containing mark, filtered, and polarised in 200 mm. tube at 20°C.

Polarisation before inversion .	+78·1
Polarisation after inversion .	−21·4
Total	99·5

$$\frac{99\cdot5 \times 100}{132\cdot6} = 75\cdot04 \text{ p.c. cane sugar.}$$

Invert sugar, ash, and water. For the determination of these, 10 grms. of the sample were made into a 100 c.c. solution, and filtered bright; the sp.gr. = 1036·45.

For the invert sugar, 10 c.c. treated with Fehling's solution gave ·241 grms. CuO (mean of two experiments); CuO per 100 c.c. = 2·41, $\frac{2\cdot41}{2\cdot205} \times 100 = 11\cdot06$ p.c. invert sugar (1 grm. dextrose or invert sugar reduces 2·205 CuO [1]).

Soluble ash. 50 c.c. were evaporated in a platinum dish along with 10 c.c. dilute sulphuric acid to dryness, the charred mass ignited and weighed; this gave ·123 grms. of ash, which multiplied by 2 = ·246 grms. per 100 c.c., or 2·46 p.c.

Insoluble ash. The residue on the filter, after being well washed with water, dried, ignited, and weighed, gave ·309 grms, or 3·09 p.c.

Water, and other organic matters not sugar. 2·46 × 8 = 1·968 degrees of gravity due to ash; this, subtracted from the sp.gr. of the solution, gives sp.gr. due to total organic matters:

$$1036\cdot45 - 1\cdot96 = 1034\cdot49 - 1000 = 34\cdot49,$$

which divided by 3·86 = 8·935, or 89·35 p.c.

$$89\cdot35 + 2\cdot46 + 3\cdot10 = 94\cdot91,$$

and this, subtracted from 100, leaves 5·09 p.c. of water. The water determined direct by drying and weighing until constant gave 7·44 p.c., which is undoubtedly too high. The other organic matters not sugar are obtained by adding the cane sugar and invert together and subtracting the sum of these from the total organic solids; thus: 75·04 + 11·06 = 86·10, and 89·35 − 86·10 = 3·25.

The analysis of this sugar will therefore stand thus:

Cane sugar	75·04
Invert sugar	11·06
Other organic matters not sugar	3·25
Ash, soluble	2·46
Ash, insoluble	3·10
Water	5·09
Total	100·00

Analysis of beet sugar. This sample, analysed in the same manner as the previous sample, gave the following results:

Cane sugar	87·33
Invert sugar	none
Other organic matters not sugar	6·27
Ash, soluble	2·77
Ash, insoluble	0·21
Water	3·42
Total	100·00

The water determined direct gave 3·10.

The effect of mineral acids (hydrochloric and sulphuric) on the specific rotation of invert sugar has already been referred to, and hence in the analysis of sugars containing an appreciable amount of invert sugar, and where great accuracy is required, Clerget's method of double polarisation is not applicable, since the addition of the acid increases the lævo- rotation of the invert sugar already present in the sample. Hence the polarisation after inversion would apparently show more cane sugar to be present than there was in reality. Therefore, in making analyses of very low-class sugars, molasses, &c., it is preferable to proceed as follows. Determine the total amount of reducing sugar after inversion by means of Fehling's solution gravimetrically, from this subtract the amount of reducing sugar, similarly determined before inversion, multiply the remainder by ·95; the result will give the amount of cane sugar present.

[illegible] 100 c.c.). Cane sugar determined by Fehling's solution:

CuO per 100 c.c. after inversion = 16·1500 = 7·321
CuO per 100 c.c. before inversion = 8·3466 = 3·785

Diff. = 3·539

3·539 × ·95 × 10 = 33·60 p.c. cane sugar;
3·785 × 10 = 37·85 p.c. invert sugar.

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[1] [illegible]

Soluble ash per 100 c.c. = ·666 ; ·666 × 8 = 5·328.

Sp.gr. of solution = 1037·03
Less 5·32
1031·71

and 1031·71 − 1000 = 31·71, which divided by 3·86 = 8·2099.

Total organic solids p.c. = 82·10, say. 82·10 − (33·60 + 37·85) = 10·65, organic matters not sugar. Water = 100 − (82·10 + 6·66) = 11·24.

The results of analysis stand thus:

Cane sugar	33·60
Invert sugar	37·85
Other organic matters not sugar	10·65
Ash, soluble	6·66
Water	11·24
Total . . .	100·00

The following analyses will give some idea of the composition of the various kinds of sugar to be met with in commerce:—

Table IX.—*Analyses of Raw and Refined Sugars and Molasses.*

Quality of sugar	Cane sugar	Invert sugar	Other organic matters	Ash, soluble	Ash, insoluble	Water
1. East India Jaggery . . .	77·35	11·06	0·95	2·46	3·07	5·11
2. West India	82·00	6·79	3·24	2·00	—	5·97
3. China	76·00	11·79	2·60	2·09	0·76	6·76
4. Unclayed Manilla	83·50	3·94	6·39	2·72	0·52	2·93
5. Mauritius	87·20	5·39	2·10	1·57	0·38	3·36
6. Java	81·06	6·14	6·09	1·93	—	5·81
7. Egyptian	88·62	4·14	0·43	3·13	—	3·68
8. Beet, 75 p.c.	92·10	0·00	0·87	3·08	0·19	3·76
9. Granulated cane	99·90	none	none	trace	—	trace
10. Tate's crystals	99·38	none	none	0·10	—	0·52
11. Sugar-house molasses . . .	43·50	15·20	5·60	10·10	—	30·64
12. Plantation molasses . . .	45·64	20·80	10·58	4·07	—	18·91

Calculation of rendement. In order to obtain the 'rendement,' or the net amount of crystallisable sugar which should be yielded by a given sample of sugar in the process of refining it is usual to assume the following:

1. That one part of soluble ash prevents the crystallisation of five parts of cane sugar.

2. That one part of invert sugar prevents the crystallisation of one part of cane sugar. Hence in practice from the amount of crystallisable sugar as determined by the saccharimeter deduct the amount of invert sugar and five times the amount of soluble ash as found by analysis; the remainder will be the net amount of crystallisable sugar or 'rendement.'

Molasses and syrups.

Quotient of purity. The various constituents, with the exception of cane sugar, are estimated in the same manner as described under raw sugar, the cane sugar being estimated by inversion and Fehling's solution.

The estimation of the quotient of purity—or, in other words, the estimation of the percentage of pure sugar contained in the dry substance, *i.e.* the total soluble matter if it were deprived of water—is of much value to the refiner, showing at a glance the proportion of pure sugar to impurities in the various stages of the process of manufacture, being altogether independent of the amount of water which may be present, the object of the refiner being not to know how much sugar is actually present in his various liquors, but how pure it is.

This is best determined by dividing the total solid matters into the percentage of pure sugar multiplied by 100; the amount of total solid matters is deduced from the specific gravity, and the percentage of pure sugar by polarisation.

33. *Analysis of Commercial Invert Sugar.* Invert sugar is now manufactured on a very extensive scale for use in brewing as a partial substitute for malt, and is sold under the names of 'invert sugar' and lævo-saccharum.'

The analysis of commercial invert sugar may be effected in a similar manner to that of raw sugars, with this exception, that the small quantity of cane sugar (about 2 p.c.) which is generally present cannot be accurately estimated by double polarisation, so that the analysis of this product does not strictly come within the province of saccharimetry. Nevertheless it has been deemed expedient for many reasons to give the method of analysis for it.

For the complete analysis of invert sugar 25 grms. of the substance are weighed out in a tared beaker, dissolved in a little warm water, transferred to a 250 c.c. flask, the rinsings from the beaker added, cooled down to 15·5°C., and made up with water to the containing mark.

The *invert sugar* is determined gravimetrically by means of Fehling's solution, 1 c.c. of the solution being taken for that purpose.

Cane sugar. 100 c.c. of solution are taken in a flask having two marks on the neck, 100 c.c. and 110 c.c., 1 c.c. of strong hydrochloric acid added, and the neck of the flask twirled rapidly between the fingers so as to mix the acid with the sugar solution. The flask is then plunged in a water-bath at 70°C. In about five minutes the temperature of the solution in the flask will have risen to 68°C., at which temperature it is maintained for five minutes longer, taken out, cooled down, and made up with water to the 110 mark; the total invert sugar is then determined gravimetrically with Fehling's solution, 1 c.c. being taken for the purpose, and the result multiplied by $\frac{11}{10}$ to correct for dilution.

The invert sugar before inversion subtracted from that found after inversion will give the amount of invert sugar due to the cane sugar which may be present; this multiplied by ·95 gives the cane sugar in the sample.

The ash is determined as for raw sugar, 50 c.c. of solution being taken for the purpose.

The water and other organic matters not sugar are estimated in the same manner as described for analysis of raw sugars.

TABLE X.—*Average Composition of Commercial Invert Sugar.*

Invert sugar	76·6
Cane sugar	2·5
Other carbohydrates	0·9
Ash	2·0
Water	18·0
Total	100·0

34. *Starch.* The estimation of starch, or of the products of the decomposition of starch, is effected in various ways according to the circumstances under which they present themselves to the analyst.

Sometimes it will be found convenient to estimate starch by inversion with diastase, as in the case of the cereals, at other times by inversion with acid, and when neither of these are admissible the starch is usually determined by difference.

35. *Estimation of starch in cereals.* For this determination O'Sullivan's method (C. J. 45, 1), which has already been referred to (*v.* STARCH), is the most accurate. The solution, having been prepared as directed on p. 590 of this volume, is proceeded with as follows:

(*a*) The specific gravity is determined at 15·5 C.

(*b*) The optical activity in 200 mm. tube is taken, and

(*c*) The cupric oxide reduction per 100 c.c. is determined. As the products of decomposition of starch with diastase can be expressed entirely in terms of dextrin and maltose, the above factors are sufficient for their estimation. The following example shows at once the method of calculating the results.

Five grms. of barley flour treated as already described on p. 590, and acted upon with 0·03 grm. diastase, gave 100 c.c. solution at 15·5 °C. having a sp.gr. = 1010·03 = 2·539 grms. of solid matter, taking 1003·95 as the sp.gr. of a solution containing in 100 c.c. at 15·5 C. 1 grm. of starch products.

9·178 grms. of this solution reduced 0·241 grm. cupric oxide, and a layer of it 200 mm. in length gave a deviation with a Soleil-Ventzke-Scheibler saccharimeter equal to 21·1 divisions. These data give

0·241 × 0·7256 (K of maltose = 62·5) = 0·1748 grm. maltose in 9·178 grms. solution.

100 c.c. solution = 101·003 grms.; hence

9·178 : 101·003 : : 0·1748 : x maltose in the 100 c.c.

$$x = 1·923.$$

The optical activity of maltose may for the concentration $c = 10$, be taken as $[\alpha]_j = +154°$ ($[\alpha]_D = +139°$), and that of dextrin $[\alpha]_j = +222°$ ($[\alpha]_D = +200·4°$). With these values, 1 grm. of maltose in 100 c.c. solution gives a deviation in a 200 mm. tube with the instrument above mentioned = 8·02 divisions, and 1 grm. of dextrin in 100 c.c. in the same length of tube 11·56 divisions. Then

1·923 × 8·02 = 15·422, the activity of the maltose;
21·1 − 15·422 = 5·678, the activity of the dextrin;
and 5·678 ÷ 11·56 = 0·491, the dextrin in the 100 c.c. solution. Hence

Maltose	= 1·923 grms. per 100 c.c.
Dextrin	= 0·491 grms. per 100 c.c.
Diastase	= 0·030 grms. per 100 c.c.
Total	2·444 grms. per 100 c.c.

Against 2·539 grms. as represented by the sp.gr.; leaving 0·095 grms. matter unaccounted for, and which is due in great part to α amylan. The maltose and dextrin only are derived from the starch; the latter without increase in weight, the former with an increase of 5·5 p.c.—*i.e.* 1 part of starch yields 1·055 parts maltose. Hence—

1·055 : 1·923 : : 1 : x starch = maltose; x = 1·522 grms. starch.

Then 1·822 grms. starch as maltose.
0·491 grms. starch as dextrin.

Total 2·313 grms. starch from the 5 grms. barley.

This equals 46·26 p.c. A second experiment with the same barley gave 46·38 p.c.

36. *Starch sugars—Glucose.* Under this head are included various products derived from starch by the action of acids, and to which the same general principles of analysis may be applied. These products are known in commerce by different names, according to their composition and mode of manufacture, and contain dextrose, maltose, and dextrin in varying proportions according to the conditions of time, temperature, and pressure under which they are manufactured (*v.* DEXTROSE, vol. i. p. 653; STARCH, this vol. p. 564).

It has been and is still the custom with many analysts to report the results of their analysis of commercial glucose in terms of dextrin and dextrose only, the latter being deduced from the cupric reducing power, thereby ignoring the presence of maltose altogether, a body which is almost invariably found to be present in all samples of commercial glucose, and consequently rendering the analysis comparatively worthless for technical purposes.

In addition to the above carbohydrates, commercial glucoses generally contain small quantities of other bodies which are unfermentable, and until very lately were supposed to possess no cupric reducing power and to exert no action on polarised light; but recent investigations show that these bodies possess both cupric reducing power and optical activity, although very little more than this has been satisfactorily proved up to the present.

In the following method for the analysis of commercial glucose the presence of all organic bodies other than dextrin, maltose, and dextrose are ignored, and consequently it cannot be regarded as an extremely accurate one, but is certainly a great improvement on the older mode of analysis, where all the cupric reducing power was attributed to dextrose.

For all practical purposes when the specific rotatory power does not exceed $[\alpha]_D = 55°$, it may be assumed that dextrin is entirely absent.

For the analysis of glucose by this method the following determinations are necessary.

(*a*) Specific gravity of 10 grms. per 100 c.c. solution.

(*b*) Specific rotatory power.

(*c*) Cupric reducing power.

(*d*) Ash.

(*e*) Moisture.

25 grms. of the sample are carefully weighed out in a tared beaker, dissolved in water, transferred to a 250 c.c. flask, and made up to the containing mark at 15·5°C.

The specific gravity, optical activity in 200 mm. tube, and cupric oxide reduction in grms. per 100 c.c. of the solution, are obtained in the usual manner, as described under section 32.

The moisture may be determined either by drying at 100°C. and weighing until constant, or may be deduced from the sp.gr. as directed under section 32. For the ash 50 c.c. of solution are sulphated, evaporated to dryness, ignited, and weighed.

The specific rotatory power $[\alpha]_D$ of the total carbohydrates present is next calculated from the optical activity; the cupric reducing power (K) is also determined. The percentage of dextrose, maltose, and dextrin may then be calculated from these factors by means of the following formulæ:

Where dextrin, maltose, and dextrose are present

$$\text{maltose} = \frac{([\alpha]_D + 1{\cdot}42\text{K} - 195)\text{S}}{27{\cdot}2},$$

$$\text{dextrose} = \frac{\text{SK}}{100} - {\cdot}61m,$$

$$\text{dextrin} = \text{S} - (g + m),$$

where S = total carbohydrates,
g = dextrose,
m = maltose,
d = dextrin.

The above formulæ are obtained as follows. It is assumed that no other organic bodies than dextrin, maltose, and dextrose are present.

1. $g + m + d = \text{S}.$
2. $100g + 61m = \text{SK}.$
3. $52{\cdot}8g + 135{\cdot}4m + 195d = \text{S}[\alpha]_D.$
4. $g = \dfrac{\text{SK}}{100} - 0{\cdot}61m.$
5. $d = \text{S} - (g + m) = \text{S} - \left(\dfrac{\text{SK}}{100} - {\cdot}61m + m\right)$

$$= \text{S} - \left(\frac{\text{SK}}{100} + {\cdot}39m\right).$$

substituting these values for g and d in equation 3:

$$52{\cdot}8\left(\frac{\text{SK}}{100} - {\cdot}61m\right) + 135{\cdot}4m$$
$$+ 195\left[\text{S} - \left(\frac{\text{SK}}{100} + {\cdot}39m\right)\right] = \text{S}[\alpha]_D$$

whence equation for maltose as above.

Where only maltose and dextrose are present,

$$\text{maltose} = \frac{\text{S}([\alpha]_D - {\cdot}528\text{K})}{103{\cdot}2},$$

$$\text{dextrose} = \frac{\text{SK}}{100} - {\cdot}61m.$$

The following examples show the method of calculation. Analysis of liquid glucose. 10 grms. per 100 c.c. solution:

$$\begin{array}{lr} & \text{Sp.gr.} = 1031{\cdot}15 \\ \text{Correction for ash} & {\cdot}17 \\ \hline & (1030{\cdot}98 - 1000) \div 3{\cdot}86 \end{array}$$

= 8·0258 total organic solid matters per 100 c.c.;
= 80·26 p.c.;

optical activity 200 mm. = 21·7;

CuO reduction in grms. per 100 c.c. = 9·00;

$$[\alpha]_D = \frac{21{\cdot}7 \times 100}{2 \times 8{\cdot}0258} = 135{\cdot}1.$$

$$\text{K} = \frac{9{\cdot}00 \times 100 \times {\cdot}4535}{8{\cdot}0258} = 50{\cdot}8;$$

$$\text{maltose} = \frac{(135{\cdot}1 + 1{\cdot}42 \times 50{\cdot}8 - 195)}{27{\cdot}2}80{\cdot}26$$

$$= 36{\cdot}10;$$

$$\text{dextrose} = \frac{1{\cdot}42 \times 50{\cdot}8}{100} - {\cdot}61 \times 36{\cdot}10 = 18{\cdot}75;$$

$$\text{dextrin} = 80{\cdot}26 - (36{\cdot}10 + 18{\cdot}75) = 25{\cdot}41;$$

ash 5 grms. sulphated gave ·0108 = ·216 p.c. say ·22;

$$\text{water} = 100 - (80{\cdot}26 + {\cdot}22) = 19{\cdot}52.$$

The analysis stands as follows:

Dextrin	25·41
Maltose	36·10
Dextrose	18·75
Ash	·22
Water	19·52
Total	100·00

In making an analysis of a sample of glucose by this method, very great care must be taken to ensure extreme accuracy in the different operations, as very slight differences in the values of K and $[\alpha]$ cause an appreciable difference in the percentage composition. As will be seen, no account is taken of the specific rotatory and cupric reducing powers of what are termed the other carbohydrates, although there can be no doubt that when they are present in appreciable quantity they must exert to a greater or less extent some influence on the values of K and $[\alpha]$.

As a rule, the glucoses made from sago and rice sent out by the English manufacturers contain very little or none of these bodies, and, where care is exercised in the analysis, fairly accurate results may be obtained by this method.

In 1882, Wiley (C. N. 46, 175) introduced an application of Knapp's mercuric cyanide reaction to the analysis of glucose, and which apparently gave very reliable results, but the value of the process is considerably discounted by the assumption that 'both dextrose and maltose when treated to saturation with reducible solutions like mercuric cyanide yield decomposition products which are optically inactive,' and that dextrin under similar circumstances is unacted upon. This assumption has not yet been proved, and, therefore, it is hardly necessary to do more than allude to the process here.

For the analysis of samples containing appreciable quantities of dextrin, such as dextrin maltose and glucose syrup, the writer has found the following method give fairly accurate results.

The specific gravity, optical activity in 200 mm. tube, and cupric oxide reduction in grms. per 100 c.c. of a 10 grm. per 100 c.c. solution are determined in the usual manner. 150 c.c. of this solution are then set to ferment with 1·5 grms. yeast at 85°F., and as soon as the fermentation has entirely ceased, which is usually at the end of three days, the fermented liquid is cooled to normal temperature, a little alumina cream added, diluted to 300 c.c., and filtered bright. The optical activity in 200 mm. tube and the cupric oxide reduction are then determined. The difference between these before and after fermentation give data whereby the dextrose and that portion of the maltose which has fermented may be determined; the remainder of the maltose and the unfermentable dextrin are also determined in the residue.

This method assumes that all the dextrose and a large proportion of the maltose undergoes fermentation, an assumption which is entirely borne out by experiment.

The following example will serve to make the method clear:

Taking the same sample as given above, 10 grms. per 100 c.c. solution.

Before fermentation:

Sp.gr. . .	= 1031·15
Correction for ash	·17

$(1030{\cdot}98 - 1000) \div 3{\cdot}86$ $= 8{\cdot}0258$; total organic solid matters per 100 c.c. $= 80{\cdot}26$ p.c.; $[\alpha]_D = 135{\cdot}1$; $K = 50{\cdot}8$.

After fermentation: Optical activity 200 mm. $= 14{\cdot}00$; CuO reduction in grms. per 100 c.c. $= 2{\cdot}11$;

$$[\alpha]_D = \frac{14 \times 100}{2 \times 8{\cdot}0258} = 87{\cdot}2;$$

$$K = \frac{2{\cdot}11 \times 100 \times {\cdot}4535}{8{\cdot}0258} = 11{\cdot}9$$

$135{\cdot}1 - 87{\cdot}2 = 47{\cdot}9 = [\alpha]_D$ of matter fermented.

$50{\cdot}8 - 11{\cdot}9 = 38{\cdot}9 =$ K of matter fermented.

Then, according to equations,

$$m = \frac{S([\alpha]_D - {\cdot}528\,K)}{103{\cdot}2}, \text{ and } g = \frac{SK}{100} - {\cdot}61\,m.$$

Maltose fermented = 19·46.

Dextrose . . = 19·35.

The remaining maltose and dextrin are calculated from the solution after fermentation as follows:

CuO per 100 c.c. = 2·11; 2·11 × ·743 = 1·5677 grms. maltose per 100 c.c. = 15·67 grms. maltose p.c.

Total optical activity 200 mm. . .	= 14·00
Optical activity due to maltose = 1·5677 × 2·708	= 4·24
Optical activity due to dextrin . .	= 9·76

9·76 ÷ 3·9 = 2·5 grms. dextrin per 100 c.c. = 25 grms. dextrin p.c.

Adding the maltose unfermented to the maltose fermented, 19·46 + 15·67 = 35·13 total maltose p.c., the results then stand as follows:

Dextrin	25·00
Maltose	35·13
Dextrose	19·35
Inert carbohydrates . .	0·78
Ash	0·22
Water	19·52
Total	100·00

The so-called inert carbohydrates are found by subtracting the sum of the dextrin, maltose, and dextrose from the total organic matter. Thus 80·26 − (25·00 + 35·13 + 19·35) = 0·78.

A slight difference will be observed between the above numbers and those obtained by the preceding method. There is every reason to believe that the latter are the more correct.

A method is given by Moritz and Morris (Science of Brewing, p. 492) in which the specific rotatory and cupric reducing powers of the other carbohydrates are taken into account. The mode of proceeding is as follows. The specific rotatory $[\alpha]_D$ and cupric reducing power (K) of the sample are determined before and after fermentation, and from the data thus obtained the respective amounts of carbohydrates (dextrose, maltose, dextrin, gallisin) that are present may be calculated.

Before fermentation. Reducing power. Take from 0·1 to 0·2 grm. (1 to 2 c.c. of 10 grms. per 100 c.c. solution), dissolve, and determine cupric oxide reducing power in the usual way.

Opticity. Take 10 or 20 grms. of the sample (10 if a dark sample, 20 if a pale one), dissolve, and determine opticity in the usual way.

Reducing power and opticity after fermentation. Take about 10 grms., dissolve in about 50 to 100 c.c. of water, add 1 grm. yeast, and 0·25 c.c. of normal cold water malt extract. To this is also added 10 c.c. of yeast water to afford nourishment to the yeast. The yeast water is prepared by stirring up some yeast (1 part) with water (10 parts), boiling, and filtering, the filtrate only being used.

The fermenting mixture is kept at 80°F. for three days, then diluted to 200 c.c., a little alumina added, and the whole filtered. The reducing power is determined in 10 c.c. of the filtrate, and its opticity is also determined in a 100 mm. tube. Example:

Reducing power before fermentation. Took 0·1201 grm. of sample; CuO obtained, 0·1747 grm. This is calculated into percentage of dextrose on sample, thus:

$$\frac{0{\cdot}1747 \times 0{\cdot}4535 \times 100}{0{\cdot}1201}$$

= 65·97 p.c. apparent dextrose.

Opticity before fermentation. Took 10 grms., dissolved in water, and made up to 100 c.c. Reading,[1] 17·4 divs. in 100 mm. tube. This is calculated into $[\alpha]_D$ thus:

$$\frac{17{\cdot}4 \times 0{\cdot}346 \times 100}{10} = 60{\cdot}2\ [\alpha]_D.$$

Reducing power after fermentation. 10 grms. taken; after fermentation, 10 c.c. of filtrate obtained as previously directed gave 0·036 grm. CuO. This is first calculated into dextrose as a percentage on sample, thus:

$$\frac{0{\cdot}036 \times 0{\cdot}4535 \times 200 \times 10}{10} = 3{\cdot}3 \text{ p.c.}$$

Opticity after fermentation. Reading in 100 mm. tube, 2·5 divs. This is calculated into $[\alpha]_D$, on sample, thus:

$$\frac{2{\cdot}5 \times 0{\cdot}346 \times 200}{10} = 17{\cdot}3\ [\alpha]_D.$$

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[1] [illegible]

The loss in reducing power and the loss in opticity after fermentation will be due to the removal of the fermentable matter, the dextrose and maltose. Hence:

Reducing power before fermentation	65·97 p.c.
Reducing power after fermentation .	3·30 p.c.
	62·67 p.c.

Opticity before fermentation . . .	60·2°
Opticity after fermentation . . .	17·3°
	42·9°

62·67 is therefore the reducing power in terms of dextrose (K) of the mixture of dextrose and maltose in the sample; and 42·9 is the opticity ($[\alpha]_D$) of this mixture. The relative proportions of dextrose and maltose can now be determined by the following simultaneous equations, where D and M represent respectively the dextrose and maltose in 100 parts of the sample.

$$(1)\quad 100D + 61M = 62{\cdot}67 \times 100.$$
$$(2)\quad 52{\cdot}8D + 135{\cdot}4M = 42{\cdot}9 \times 100.$$

These equations give:

$$D = 56{\cdot}88.$$
$$M = 9{\cdot}50.$$

The percentage of dextrose in the sample is therefore 56·88, and the percentage of maltose 9·50.

The gallisin is found from the reducing power of the solution after fermentation. The gallisin, calculated in terms of dextrose, was 3·3. Since the K of gallisin is about 45, the true percentage of gallisin can be found by multiplying the above figure by $\frac{100}{45}$; thus

$$\frac{3{\cdot}3 \times 100}{45} = 7{\cdot}33.$$

The dextrin is calculated as follows: the opticity due to the percentage of each of the other carbohydrates found is calculated, and the whole added together; the difference between this number and the opticity of the original sample will be due to dextrin. Thus—

Dextrose, 56·88 . .	$56{\cdot}88 \times 0{\cdot}528$[1]	= 29·97
Maltose, 9·50 . . .	$9{\cdot}50 \times 1{\cdot}36$	= 12·93
Gallisin, 7·33 . . .	$7{\cdot}33 \times 0{\cdot}84$	= 6·16
		49·06

Opticity of original sample . .	60·2°
Opticity due to carbohydrates determined	49·06°
	11·14°

The opticity due to dextrin is therefore 11·14°, and $\frac{11{\cdot}14}{1{\cdot}95} = 5{\cdot}71$ = percentage of dextrin.

The determinations of ash, albuminoids, water, and inert carbohydrates are carried out in the same manner as already described.

In this case they came out as follow: ash, 1·87; albuminoids, 1·62; water, 15·02; inert carbohydrates, 2·07 p.c. The analysis would therefore stand as follows:

Dextrose	56·88
Maltose	9·50
Dextrin	5·71
Gallisin	7·33
Ash	1·87
Albuminoids	1·62
Water	15·02
Inert carbohydrates . . .	2·07
	100·00

37. *Estimation of starch by inversion with hydrochloric acid.* Where hydrochloric acid is used for transforming the starch instead of diastase, the products of the decomposition will consist of dextrin, maltose, and dextrose. For the determination of these the following operations are necessary:

(*a*) Specific gravity of the solution at 15·5°C.

(*b*) Optical activity in 200 mm. tube.

(*c*) Cupric oxide reduction in grms. per 100 c.c.

(*d*) Fermentation of the solution at 85°F.

(*e*) Optical activity in 200 mm. of residue.

(*f*) Cupric oxide reduction in grms. per 100 c.c.

(*g*) Ash (before fermentation).

Before setting the solution to ferment, the acid must be neutralised with sodium carbonate. The analysis is then conducted by one of the methods described above.

38. *Commercial dextrin, or British gum.* In the analysis of commercial dextrin the following substances have to be determined: 1. Starch. 2. Dextrin. 3. Maltose. 4. Ash. 5. Moisture. 6. Acidity.

The estimation of the portion soluble in cold water is made by dissolving 25 grms. of the sample in cold water, transferring to a 500 c.c. flask, making up to the containing mark with water at 15·5°C., allowing to stand some time, and filtering.

The dextrin, maltose, and dextrose (if any) are then determined by any of the methods already given. Dextrose is generally absent, and where present exists in such small quantity that it may be, for all practical purposes, regarded as maltose, and estimated as such.

The portion soluble in cold water, which consists almost entirely of starch, is well washed with water, transferred to a small beaker, and determined by O'Sullivan's diastase method (section 35).

In cases where the amount of insoluble starch is large a correction should be made for the volume of the same. Taking the sp.gr. of starch as 1·6, the number of c.c. to be deducted is found by dividing the amount in grms. of insoluble matter in 25 grms. of the sample by 1·6; thus the volume to be deducted for 40 p.c. of starch will be 6·2.

The water may be determined by drying at 105°C., and the ash in the usual manner.

The difference between 100 and the sum of the maltose, dextrin, starch, moisture, and ash gives the percentage of the other organic matters.

39. *Determination of dextrose in diabetic urine.* The polarimeter may be very usefully applied to the determination of dextrose in the

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[1] These factors, 0·528, &c., express the opticity α_D given by the respective carbohydrates when 1 grm. of each is dissolved in 100 c.c. and the reading taken in the 100 mm. tube.

urine of diabetic patients, and although the results are not quite so accurate perhaps as those obtained gravimetrically with Fehling's solution, owing to the presence of other optically-active bodies, as well as of bodies, which, although themselves inactive, yet exert a certain influence on the rotatory power—for instance, acetone, which is sometimes present, increases the rotatory power to a slight extent, whilst, on the other hand, urea, ammonium salts, and phosphates decrease the rotatory power slightly (Pribram, M. 9, 395)—nevertheless, as a means of recording comparative results, the polarimetric method is exceedingly convenient and fairly reliable. 100 c.c. of the urine are taken, and if not already acid should be rendered slightly so with acetic acid, and heated to boiling, cooled, made up to volume with distilled water, and filtered bright, then polarised in a 200 mm. tube, and the readings recorded daily or from time to time.

40. *Examination of honey.* Genuine honey consists principally of invert sugar (about 65–80 p.c.), the other constituents being water, wax, pollen, mineral matters, organic acids, &c. The analysis of honey may be performed in a manner similar to that given for invert sugar; frequently cane sugar, glucose syrup, molasses, and invert sugar are added as adulterants. These may, however, be readily detected by a careful examination of the sample by means of the polarimeter and Fehling's solution combined. Another means by which adulteration may be detected is by causing a solution of the sample to undergo fermentation by the addition of yeast, and polarising the residue. The residue from the fermentation of genuine honey does not show a greater specific rotatory power than about 2° either to the left or right. By this means the addition of starch sugar can be readily detected. Hehner (An. 9, 64) recommends, in testing the genuineness of honey, to determine the moisture and the reducing sugars, both before and after fermentation. According to him, the amount of moisture in genuine honey should not exceed 23 p.c., and the amount of reducing (invert) sugar should not be sensibly greater after inversion than before; also, after fermentation with yeast the total solid matters, less the p.c. of unfermented reducing sugar, should not exceed 5 p.c. The polarisation after fermentation should equal 0, a lævo- rotation indicating that the honey had become crystalline in the comb, whilst a dextro-rotation points to adulteration with starch sugar. When this is the case, dextrin should be looked for with the alcohol test, and sulphuric acid (from the sulphate of lime always found to be present in commercial glucose) tested for with barium chloride. Neither alcohol nor barium chloride should give any appreciable amount of precipitate with genuine honey. The following table shows the difference between the genuine and adulterated article.

TABLE XI. *Analyses of Genuine and Adulterated Honey (Hehner).*

—	I. Moisture p.c.	II. [illegible] p.c.	III. 100 – (I. + II.)	[illegible]	Polarisation of 10 p.c. [illegible]	Glucose p.c. after fermentation	Polarisation of 10 p.c. solution in [illegible]	Total solid matters p.c. after fermentation
GENUINE HONEY								
Narbonne . .	15·09	73·46	11·45	73·60	+ 1 div.	1·89	+ 2	5·75
American orange blossom . .	17·33	70·94	11·73	70·87	– 2 ,,	—	—	—
English . .	21·04	64·50	14·46	64·44	0 ,,	—	—	—
English . .	18·37	68·65	13·18	68·30	+ 1 ,,	2·55	+ 2	6·29
ADULTERATED .	17·54	48·45	34·01	48·33	+ 50 ,,	9·02	+ 30	31·45

41. Starch sugar or glucose is frequently added in America as an adulterant to sugar-house molasses, syrups, preserved fruits, &c. According to Casamajor (C. N. 44, 265), the presence of glucose in sugar-house molasses may be easily detected by the saccharimeter. When the syrup has the usual density of about 40°B., and when starch sugar has been added in the usual proportions, 26·048 grms. of the sample are made into 100 c.c. solution and polarised. This should show a percentage not higher than the number of Baumé degrees indicating the density—for instance, cane sugar molasses of 40 B. has the following composition:—

Sugar	37·5
Soluble impurities	37·5
Water	25·0

If direct polarisation should indicate 55 p.c. of sugar, and if the molasses were unadulterated, the composition would be, according to this:—

Sugar	55
Soluble impurities.	20
Water	25

But a product of this composition would not be a clear syrup at 40 B., but a mixture of syrup and crystals. Therefore, if the product is a clear syrup at 40 B., and it polarises 55 p.c., this cannot consist entirely of cane sugar.

As a check, however, upon this, it is best to resort to double polarisation, when the presence of starch sugar may be placed beyond a doubt in an adulterated sample.

Crystallised glucose, or glucose, freed from moisture and reduced to powder is sometimes mixed in comparatively large proportions with refined sugars. This may be detected by double polarisation. For instance, a sample of dry sugar which showed 97 p.c. by direct polarisation after inversion gave a reading of only –9·8, instead of –31·5, were the sugar unadulterated; from these numbers the percentage of cane sugar would appear to be 80 p.c. As the sugar was practically dry, the difference between 80 and 100 may be taken to represent the quantity of starch sugar which had been added.

42. *Examination of chocolate, candies, &c., confectionery for cane sugar.* The examination of these substances is made with a view to detecting any adulteration of the cane sugar entering into their composition with starch, sugar, or honey. The following instructions for the examination of these substances have been issued by the Association of Official Agricultural Chemists, U.S.A. (*v. C. N.* 66, 94).

The Soleil-Ventzke saccharimeter is used in the sucrose determinations.

In all cases where the substance to be examined contains no other optically active bodies, the direct polarisation will give accurate results. If such are present—as, for instance, glucose, invert sugar, maltose, dextrin, pectinous bodies—the application of the polariscope becomes uncertain, and only in a few cases, which will be given below, can somewhat reliable results be obtained.

As regards the preparation of the solutions the following must be remembered:—Material which consists mostly of sucrose, and leaves only a small residue on being treated with water, can be weighed out in the dish, and the solution immediately transferred to the sugar flask. When the substance, however, contains much insoluble matter, the latter should not be washed into the flask, as the volume of the sugar solution in such a case would be less than 100 c.c. In this case the residue must be separated from the solution by filtration and washing. Generally, the sugar solution is not quite transparent, and must be treated with some clearing agent. The solutions serving this purpose are:—

1. Lead acetate, of which from 1 to 10 c.c. are mixed with the solution, and the latter filtered after standing from fifteen to thirty minutes.

2. Lead acetate with subsequent addition of alum or aluminium sulphate, the lead sulphate formed carrying down the foreign matter.

3. Aluminium hydrate in the form of a thin paste, of which several c.c. are shaken with the solution.

4. Tannic acid, to precipitate albuminous substances. This must be examined beforehand with regard to its optical activity.

5. Charred blood or bone-black, to remove colouring matter, $\frac{1}{2}$ to 1 grm., are added to the liquid.

In some cases this clearing is difficult, and the method best adapted must be determined by previous experiments. For solutions prepared from candies the pasty aluminium hydrate is the best medium.

When, as is often the case, invert sugar is present, the result of the direct polarisation will be too low, on account of the left-handed rotation of this sugar. In such a case Clerget's inversion method must be applied to find the correct p.c. of sucrose.

If the liquid is coloured, it is shaken with $\frac{1}{2}$ to 1 grm. of bone-black, and filtered through a double filter. It is then polarised in a 200 mm. tube, which is provided with a thermometer. As the rotatory power of invert sugar is much influenced by the temperature, this factor must be regarded. The reading is best taken at 20°C., and the temperature accurately determined. The reading must also be doubled on account of the dilution of the liquid.

To calculate percentage of sucrose (R) the two readings are added together, the sum (S) multiplied by 100, and divided by 132·6.

If very much invert sugar is present, both the direct and indirect readings must be taken at the same temperature.

43. *Chocolate.* Weigh out in a German silver dish 13·024 grms. of the rasped chocolate, moisten with alcohol (to aid the solution in water), add 30 c.c. of water, and heat for ten to fifteen minutes on the water-bath. Filter while warm into a 100 to 110 c.c. flask, using a folded filter, any turbidity of the filtrate not being of any consequence. The residue on the filter is washed with hot water until the filtrate amounts to about 100 c.c. Five c.c. of lead acetate are then added, the liquid allowed to stand fifteen minutes, and a few drops of alum solution and some moist aluminium hydrate added. The liquid is then made up to 110 c.c., shaken well, and filtered through a folded filter. Slight moistening of the filter will aid filtration, but the first 25 c.c. of filtrate should then be rejected. The polarisation should be increased by one-tenth and then doubled.

44. *Candies and Confectionery.* (*a*) *Dragées* (seeds or kernels coated with sugar and flour). 26·048 grms. are covered in a beaker with 40 to 50 c.c. of water, and allowed to stand, stirring now and then, until the mass is completely saturated. If the liquid shows an acid reaction, some precipitated calcium carbonate or a few drops of ammonia are added. The larger particles are now separated by filtering through cloth, the filtrate being collected in a 100 to 110 c.c. flask. The residue on the filter is washed with cold water until about 100 c.c. of the filtrate have accumulated. Some aluminium hydrate is then added to clear it, the solution made up to 100 c.c. with water, and about half a grm. of bone-black added in case the liquid is coloured. It is then allowed to stand half-an-hour, with occasional shaking. The solution is finally filtered through a dry folded filter.

A preliminary test for invert sugar is made with Fehling's solution, and the liquid analysed accordingly. Dragées almost always contain invert sugar.

(*b*) *Raffinade wafers* (cane sugar, with ethereal oils and colouring matter). 26·048 grms. dissolved in water, made up to 100 c.c. in flask, and, if necessary, decolourised with bone-black. A preliminary test for invert sugar must always be made, and the analysis directed accordingly.

(*c*) *Santonin wafers* (worm wafers, cane sugar, with santonin and some agglutinant, as egg albumen). 13·024 grms. dissolved in a 100 c.c. flask (the santonin being insoluble), 5 c.c. of lead acetate added, with a few drops of alum solution, the solution allowed to stand some time, with occasional shaking, made up to 100 c.c., and filtered.

(*d*) *Dessert bonbons* (fondants, pralines, chocolate bonbons, consisting of cane sugar or invert sugar, serving as a covering for marmalade, fruit, or chocolate). 13·024 grms. are treated with water and a few drops of ammonium hydrate until dissolved. If only a slight residue remains, the whole can be immediately transferred to a 100 c.c. flask, otherwise it must first be filtered. One-half of the liquid is inverted, the other polarised directly after having been cleared by means of aluminium hydrate in a 50 to 55 c.c. flask.

(*c*) *Marzipan masse* (cane sugar, with crushed almonds). 13·024 grms. material are triturated in a porcelain mortar with cold water, then mixed in a flask with 50 c.c. of water and about 30 c.c. of pasty aluminium hydrate, well shaken, and filtered into a 200 c.c. flask. The residue on the filter is washed with water until the filtrate amounts to 200 c.c. As this candy contains no invert sugar, the solution can be polarised directly in the 200 mm. tube, the reading being multiplied by 4 to correct for the dilution.

(*f*) *Cakes and sweetened pastry.* 26·048 grms. of the powdered material are mixed in a flask with about 75 c.c. alcohol (85 to 90 p.c.) and allowed to stand half an hour in a warm place. It is then filtered through a fine cloth filter, and the residue washed several times with alcohol. The filtrate is collected in a porcelain dish, and heated on the water-bath until the alcohol has all been driven off. One half grm. bone-black is then added, and the solution filtered into a 100 c.c. flask. 50 c.c. are used for inversion, the remainder polarised directly.

(*g*) *Sugar-coated and preserved fruits* (marmalade, compotes, jellies). A considerable amount of invert sugar and pectinous bodies are always present. The aqueous solution of the latter has no rotatory power. If the material is solid in consistence, a crushed or finely-cut average sample must be prepared. 13·024 grms. are then mixed with 30 to 50 c.c. of water, and a few drops of ammonium hydrate (to neutralise any free vegetable acids), and allowed to stand several hours. It is then passed through a cloth filter into a 100 or 200 c.c. flask, the residue washed several times with hot water, and about 10 c.c. of aluminium hydrate and one half-grm. bone-black added to the filtrate. It is then shaken and made up to the mark. After filtering, the filtrate is polarised according to Clerget's method.

Fruit jellies and marmalade are analysed in a similar manner.

If the sucrose in the articles enumerated under section 44 *g* were calculated by the formula

$$R = \frac{100S}{142{\cdot}6 - \frac{1}{2}t},$$

there would only be obtained the percentage present at the time of analysis. The acids of the fruit have, however, converted a large amount of the cane sugar originally used into invert sugar. The original percentage of cane sugar can be calculated from the reading of the inverted solution. If this reading is referred to 26·048 grms. material dissolved in a 100 c.c. and polarised in a 200 mm. tube, the following relations will hold if the above figure be called B:

A solution of 26·048 grms. of cane sugar in 100 c.c. has, after inversion, at the temperature $t°$ the left-handed rotation $42{\cdot}6 - \frac{1}{2}t$. The amount of cane sugar corresponding to the observed polarisation B can thus be calculated by the proportion—

$$42{\cdot}6 - \tfrac{1}{2}t : 26{\cdot}048 = B : \frac{26{\cdot}048\,.\,B}{42{\cdot}6 - \frac{1}{2}t},$$

and this is contained in 26·048 grms. of the material used. Therefore the original percentage r of cane sugar can be calculated from the second proportion.

$$26{\cdot}048 : \frac{26{\cdot}048\,.\,B}{42{\cdot}6 - \frac{1}{2}t} = 100 : r$$

whence—

$$r = \frac{100\,B}{42{\cdot}6 - \frac{1}{2}t}.$$

If 13·024 grms. substance were used and the solutions polarised at exactly 20°C., then the following formula is more accurate:—

$$r = \frac{100B}{42{\cdot}6 - 10} = 3{\cdot}067\ B.$$

45. *Liquors.* The percentage of sugar in liquors is generally expressed as grms. per litre.

Every liquor must be previously tested for invert sugar by means of Fehling's solution. If no change occurs upon heating, cane sugar only is present; a yellow or red precipitate indicates the presence of other sugars.

Liquors which do not contain invert sugar may be polarised directly in the 200 mm. tube, being previously decolourised with bone-black if necessary. If a high percentage of sugar is present, the polarisation must be made in the 100 mm. tube.

The presence of the alcohol has no influence on the reading. The ethereal oils which are present, although optically active, exist in such small quantities as to be without influence. The grms. per litre (R) are found, when A is the reading in a 200 mm. tube, by $R = 2{\cdot}6048A$.

When invert sugar is present the alcohol must be removed, as it materially changes the rotation of this sugar.

Fifty c.c. of liquor are measured into a porcelain dish and evaporated to about one-half the volume on a water-bath. If the liquid has an acid reaction, a few drops of ammonium hydrate must be added before heating it. The residue is washed into a 100 c.c. flask and made up to the mark with water. One-half is then polarised directly, the other after inversion. Both solutions may have to be decolourised with bone-black.

Suppose—

V = number of c.c. used for analysis,
A = direct reading,
B = reading of inverted solution (both read in 200 mm. tube),
t = temperature of inverted solution when polarised,

then the grms. of cane sugar (R) in a litre may be calculated from the formula—

$$R = \frac{26048\,(A - B)}{(142{\cdot}6 - \frac{1}{2}t)\,V},$$

where, when the direct reading was +, the inverted reading –, the difference A - B becomes A + B.

If the temperature was exactly 20°C.—

$$R = 196{\cdot}4\,\frac{A - B}{V}.$$

In the case of liquors in which the addition of fruit juices may have caused inversion of a part of the cane sugar originally added, the original percentage of cane sugar is then calculated from the inverted reading just as for candied fruits. The grms. of cane sugar (r) per litre are found from

$$r = \frac{26{\cdot}048\mathrm{B}}{(42{\cdot}6 - \frac{1}{2}t)\mathrm{V}}, \text{ or, when } t = 20^\circ,$$

$$r = \frac{26{\cdot}048\mathrm{B}}{32{\cdot}6\mathrm{V}} = 799\,\frac{\mathrm{B}}{\mathrm{V}}.$$

46. *Analysis of wine.* Natural wine is the completely fermented product of the pure must from particular growths, without any addition of foreign material.

Made up or mixed wine is a completely fermented mixture of uncertain origin obtained by the addition of different kinds of grapes or must to stronger wine, or by the addition of sugar and the employment of certain processes.

Artificial wine is a vinous drink prepared with the partial or complete exclusion of grape juice.

In the complete analysis of a red wine, the sp.gr., alcohol, extract, ash, glycerin, unfermented sugar, total acidity, potassium bitartrate, free tartaric acid, malic acid, succinic acid, acetic acid, sulphate of lime, sulphuric acid, added sugar, phosphoric acid, colouring matter, salicylic acid, and nitrogen would be estimated.

Such an exhaustive examination as this is but rarely carried out, and only for some special purpose, for since wine has now undoubtedly become a product of manufacture, the aim of the producer being to keep the alcohol and extractive matters fairly constant from year to year, and with this object in view having recourse when necessary to the addition of artificial must, as well as saccharine and other matters, the practical bearing of some of the constituents now found in wine has become exceedingly doubtful, so that the complete examination of a wine according to fixed analytical methods and data has become almost an impossible, as well as a tedious and unnecessary, task. So that for all practical purposes, the following determinations suffice.

The original gravity, from which may be deduced the percentages of alcohol, extractive matters, and the specific gravity of the must prior to fermentation. For the method of determining the original gravity *v.* section 49, *Analysis of beer*.

Glycerin. According to Allen (Commercial Organic Analysis, p. 80), this is best done as follows: 100 c.c. of the sample of wine are evaporated to one-third in a porcelain dish, slaked lime added till the liquid is slightly alkaline, and the evaporation completed. The residue is boiled with rectified spirit, which dissolves the glycerin and leaves the succinic acid and sugar as insoluble lime compounds. The alcoholic solution, when filtered and evaporated cautiously, leaves the glycerin in a moderately pure state. In wines adulterated with starch sugar, and in other cases if accurate results are required, the glycerin obtained as above should be dissolved in absolute alcohol, and the filtered solution treated with $1\frac{1}{2}$ measures of ether. Certain impurities are precipitated by this menstruum, and the filtered solution on evaporation leaves the glycerin in a state of tolerable purity. Pure Rhenish and French wines tested by this method show a proportion of glycerin ranging from 0·7 to 1·3 p.c., and as the ratio of alcohol to glycerin in genuine wine is tolerably constant, the method sometimes serves for the detection of added alcohol or glycerin, or the recognition of the sample as factitious.

From the results obtained by Fresenius and Borgmann (Zeit. Anal. Chem. 22, 46) in the analysis of certain pure wines, white and red. The average mutual relations of some of the constituents were found to be as follows:

Alcohol to glycerin = 100 : 10·5.
Ash to extractives = 1 : 112.

From a number of experiments, Borgmann concludes that the proportion of glycerin to alcohol in pure wines is never less than 7·8 to 1,000.

The ash, the determination of which in a wine is useful as affording indications of the addition of certain mineral salts, is carried out in the usual way, 50 c.c. of wine being taken for the purpose.

In wines which have been 'plastered' (Allen, Commercial Organic Analysis) much of the acid potassium tartrate is converted into free tartaric acid, the proportion of potassium sulphate being correspondingly increased. In unplastered wine the sulphates, calculated as K_2SO_4, do not exceed 0·58 grm. per litre. By the French law, the proportion of sulphates calculated as potassium sulphate is limited to 2 grms. per litre, a regulation which is intended to prevent an excessive use of plaster.

In white wines the sulphates may be estimated directly by precipitating 100 c.c. with barium chloride after the addition of hydrochloric acid, heating to boiling, filtering, igniting, and weighing the precipitate as barium sulphate. In the case of highly-coloured wines Allen recommends the addition of a slight excess of lime-water to 100 c.c. of wine, diluting to 200 c.c., filtering through a dry filter, and precipitating the sulphates in 100 c.c. of the filtrate, after acidulation with hydrochloric acid.

Sugar. The unfermented sugar in genuine wine is wholly glucose or invert sugar, and is present in very small proportions, causing a deviation of not more than 1° or 2° on the saccharimeter either to the right or left, but more usually to the left. For the detection of cane sugar added to wine subsequent to fermentation, or of glucose added to the must, the polarimeter may be very usefully applied. For this purpose 150–200 c.c. of the liquid under examination are taken and decolourised by means of animal charcoal or basic lead acetate, and the optical activity taken in 200 mm. tube at the same time. The reducing sugar is determined in the usual way, by means of Fehling's solution. The saccharimetric examination may reveal one or other of three conditions.

(a) The deviation may be to the right, or (b) to the left, or (c) there may be no deviation, according to the nature and relative quantities of carbohydrates in solution, such as cane sugar and invert sugar, or dextrin maltose and dextrose (from commercial glucose). It is not usual to find all of these sugars present in any one sample of wine, as either cane sugar or glucose may have been added, but never both together.

The relative proportions of these sugars may be determined as follows: 50 c.c. of the wine (previously decolourised) are introduced into a 100 c.c. flask, 1 c.c. hydrochloric acid (sp.gr. 1·090) added, and water to about 75 c.c., the mixture is then plunged in a water-bath at a temperature of 70°C., at which temperature it is maintained for ten minutes, then taken out, cooled down quickly, and made up to the containing mark with distilled water at 15·5°C. and polarised. Any cane sugar that may have been present will have been inverted, and may be determined according to the Herzfeld-Clerget formula, or by means of Fehling's solution. Of course, no difference in rotation will indicate the absence of cane sugar. In this case the reducing sugar, if any, will be due to unfermented glucose, a certain amount of which is probably derived from the original must, the remainder being due to commercial glucose or starch sugar added at some stage of the manufacture, the amount of which may be calculated by any of the methods given for commercial glucose, due allowance, of course, being made for the amount of unfermented reducing sugar naturally present in the wine. When starch sugar has been added, the wine will always show a dextro- rotation in the saccharimeter, so that if cane sugar has been proved to be absent it may safely be concluded that the dextro- rotation is without doubt due to starch sugar.

47. *Analysis of malt, malt wort, and beer.* In addition to the starch contained in malt there exist also the ready-formed sugars, cane sugar, maltose, dextrose, and lævulose, organic acids, certain nitrogenous bodies, and mineral salts, all of which become soluble in both cold and hot water.

In most of the existing methods of analysis the presence of these ready-formed sugars in malt, amounting to about 12 p.c., is altogether ignored, so that a series of errors is thereby introduced which for all practical purposes renders such analyses utterly worthless. A more reliable method, and one most nearly approaching to accuracy, is the one introduced by Heron a few years ago (S. C. I. 7, 259), and which is based upon the investigations of O'Sullivan upon the starches and sugars of the cereals (C. J. 45, 1; 49, 58).

This method takes cognisance of the ready-formed sugars in malt, and shows how they may be determined with at any rate a close approximation to accuracy, and provides for an exceedingly accurate means of determining the exact proportions of maltose and dextrin derived from the starch contained in the malt during the process of mashing.

The principle of the method is as follows: A cold-water mash of the malt is first made; this extracts from the malt the ready-formed sugars, the acids, the soluble nitrogenous bodies, and the soluble mineral salts, colouring matters, &c., the various proportions of which can be then estimated.

The malt is next mashed with hot water under standard conditions. The wort from this will contain, in addition to the products derived from the starch, all the bodies soluble in cold water, so that by subtracting from the total solids contained in the solution from the hot mash all those contained in the cold mash, the remainder will obviously be only the products derived from the starch during the process of mashing. For the complete analysis of a sample of malt by this method the following operations are necessary:

I. *Preparation of hot-water mash.*

Determination of—
a. Specific gravity.
b. Optical activity in 200 mm. tube.
c. Cupric oxide reduction in grms. per 100 c.c.

II. *Preparation of cold-water mash.*

Determination of—
a. Specific gravity.
b. Optical activity in 200 mm. tube.
c. Cupric oxide reduction in grms. per 100 c.c. before inversion with invertase.
d. Cupric oxide reduction in grms. per 100 c.c. after inversion with invertase.
e. Total nitrogen.
f. Ash.

III. *Determination of moisture.*

The mode of procedure is as follows:

Cold-water mash. 50 grms. of finely-ground malt are carefully weighed out and introduced into a beaker, 500 c.c. of distilled water at 15·5°C. are poured upon it, the whole well stirred up and set aside to digest in the cold for about three hours, occasionally agitating the mixture; at the end of this period, the mash is thrown upon a filter; the filtrate does not usually come through bright at first, therefore it must be returned on the filter until it does, or it may be passed through fresh filter-paper.[1] 100 c.c. of this solution will contain all the constituents of 10 grms. of malt other than the starch products—that is to say, the various sugars already present in the malt—such as dextrose, lævulose, maltose, and cane sugar; it will also contain the various soluble albuminoids, acids, mineral salts, colouring matter, &c.

Hot-water mash. 50 grms. of the same finely-ground malt are carefully weighed out and introduced into a flask graduated to contain 515 c.c.; water, at a temperature of 72°C., is added until the mixture in the flask equals about 450 c.c. The temperature of the resulting mash, which at first may be about 64-65°C., runs up in a minute or two to 66°C., at which temperature it must be maintained for one hour in a water-bath at 66°C., furnished with a Page's regulator, so as to keep up a constant and unvarying degree of heat. Whilst this is going on, 300 c.c. of the cold mash are also digested for one hour at the same temperature. It will be well to note that immediately the filtration of the cold mash is finished, it ought to be transferred without delay to the digester, as, if left lying about too long in the laboratory (say over night), it is apt to become decomposed through bacterial fermentation. As soon as the hot mash is completed, the flask is taken out of the digester and cooled down to 15·5°C., made up with distilled water to the containing mark, well shaken up, and thrown on a linen filter, so as to strain the liquor off. 300 c.c. of this are next transferred to a boiling flask, raised quickly to boiling, and kept so for fully fifteen minutes, so as to coagulate albuminous matter &c.

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[1] [illegible] extent with the necessary corrections to be applied to the hot mash, as will be seen more clearly later on.

On cooling it is made up again to exactly 300 c.c. and filtered bright.

At the same time the cold mash is also raised quickly to boiling-point, and kept boiling for the same time as the wort from the hot mash, cooled down, made up to volume with water, and filtered bright.

Both solutions are now ready for analysis. The specific gravity, optical activity in 200 mm. tube, and cupric reducing power per 100 c.c. are determined for both the hot and cold water mashes. The amount of cane sugar in the cold mash is also estimated by inversion with invertase in the manner as described under section 31, and when a very complete analysis is required, the ash, albuminoids, and acid as lactic acid, are determined in the cold mash; the moisture contained in the malt is also estimated.

Hot mash filtrate contains 10 grms. of malt extract per 100 c.c.

Sp.gr. = 1027·52
Optical activity 200 mm. = 16·3
CuO reduced in grms. per 100 c.c. = 6·575

Cold mash.

Sp.gr. = 1008·72
Optical activity 200 mm. = 1·8
CuO reduced in grms. per 100 c.c. = 1·6

From these data may be calculated the starch products. The degrees of gravity of the cold mash subtracted from the degrees of gravity of the hot mash give the degrees of gravity due to the products of the transformation of the starch contained in the malt. Thus

$$\begin{array}{r} 1027{\cdot}52 - 1000 = 27{\cdot}52 \\ 1008{\cdot}72 - 1000 = 8{\cdot}72 \\ \hline 18{\cdot}80 \end{array}$$

= degrees of gravity due to starch products only.

18·8 ÷ 3·86 = 4·8705 grms. of solid matter (dextrin and maltose) per 100 c.c.

Optical activity 200 mm. = 16·3 − 1·8 = 14·5 due to starch products.

CuO per 100 c.c. = 6·575 − 1·6 = 4·975 = CuO reduced in grms. per 100 c.c. by starch products.

As this can be due only to maltose, the dextrin having no reducing power, the amount of maltose in grms. per 100 c.c. is arrived at as follows:

1 grm. dextrose reduces 2·205 grms. CuO, and as maltose has only the $\frac{61}{100}$ths reducing power of dextrose, therefore 1 grm. maltose reduces $\frac{61}{100} \times 2{\cdot}205 = 1{\cdot}345$; hence 4·975 ÷ 1·345 or multiplied by its reciprocal ·743 = 3·6964 grms. maltose per 100 c.c.

Having obtained the maltose, the dextrin is next calculated from the optical activity. From Table VI. it will be seen that 1 grm. maltose per 100 c.c. observed in 200 mm. tube = 2·708 angular degrees for ray D. Similarly 1 grm. dextrin per 100 c.c. = 3·9.

Hence 3·6964 × 2·708 = 10·01, opticity due to 3·6964 grms. maltose per 100 c.c. This, subtracted from total opticity of starch products, gives opticity due to dextrin 14·5 − 10·01 = 4·49, and this, divided by 3·9 = 1·1513 grms. dextrin per 100 c.c.

Therefore a hot mash made from the sample of malt in question gave

3·6964 grms. maltose per 100 c.c.
1·1513 „ dextrin „ „
4·8477 grms. total starch products per 100 c.c.

It will be noticed that there is a slight difference between the number obtained in this manner and that derived from the specific gravity.

By sp.gr.	= 4·8705
By direct analysis . . .	4·8477
Difference	·0228

This is due to the fact that the ash and albuminoids extracted in the cold mash are always slightly lower than the amount of these bodies extracted in the hot mash.

It has been observed by the writer that this difference varies very considerably with different malts, and may be regarded to a certain extent as an index of the quality of the malt: the less this difference the better the quality of the malt. Very bad malts, as a rule, show a large difference, sometimes amounting to as much as ·3 grms. per 100 c.c.

Having determined the amount of dextrin and maltose in the hot mash, the amount of starch may easily be arrived at, if thought necessary.

Attention may now be turned to the constituents of the cold mash. It will be seen already that this solution possesses both optical activity and cupric oxide reducing power, both of which are derived from sugars already present in the malt, and which have in great measure been derived from the starch during the process of germination of the barley on the malting floors.

These sugars have been found by O'Sullivan (C. J. 49, 58) to consist of cane sugar, maltose, dextrose, and lævulose in varying proportions. Taking the mean of the results obtained by O'Sullivan from the analyses of over twenty samples of malt from various sources, the following numbers are obtained:

Cane sugar	4·40
Maltose	3·15
Dextrose	2·25
Lævulose	1·10
Total	10·90

The only one of these sugars which may be determined with any degree of accuracy is cane sugar, by means of inversion with invertase; the others can only be arrived at indirectly, as follows. It is assumed that the average value for K (cupric reducing power) is represented by a number calculated from the averages given for the reducing sugars already formed in the malt; from the numbers given above this is found to be K = 81. Therefore, 1 grm. of ready-formed reducing sugars in malt will reduce an amount of CuO equivalent to $\frac{81}{100} \times 2{\cdot}205 = 1{\cdot}786$.

In the sample of malt given as an example, the CuO reduced in grms. per 100 c.c. in the cold mash was 1·6. Therefore, 1·6 ÷ 1·786 or multiplied by the reciprocal of this ·56 = ·896 grms. reducing sugars per 100 c.c.

The amount of cane sugar is found by inversion by means of invertase (see section 31). In this case the amount of CuO reduced in grms. per 100 c.c. in the cold mash after inversion was . . . . 2·653

CuO reduced in grms. per 100 c.c.
in same before inversion . 1·600

Difference . . . = 1·053

This multiplied by ·4535 = ·4775 grms. invert sugar, which multiplied by ·95 = ·4536 grms. cane sugar per 100 c.c. in cold mash.

Ash. 50 c.c. of the cold mash were evaporated to dryness, ignited, and weighed. Weight of ash = ·0549 grms. = ·1098 grms. per 100 c.c.

The *nitrogen* in 20 c.c. of cold mash determined by Kjeldahl's method amounted to ·0119 grms.; per 100 c.c. = ·0595 grms.; this multiplied by 6·25 = ·372 grms. albuminoids per 100 c.c.

The total acid in malt, which is generally expressed in terms of lactic acid, may be determined in the cold mash, 100 c.c. being taken for the purpose.

In the present instance 100 c.c. required $11{\cdot}5\,\frac{n}{20}$ ammonia and 11·5 × ·0045 = ·0517 grms. acid per 100 c.c.

The results of the examination of the cold mash stand as follows:

Sp.gr. . . . . . = 1008·72

This corrected for gravity due to
ash ·1098 × 8 . . . . = ·87

Sp.gr. corrected . . = 1007·85

This divided by 3·86 = 2·0337 grms. per 100 c.c. total organic solid matters.

Cane sugar . . = ·4536 grms. per 100 c.c.
Other sugars . . = ·8960 „ „
Albuminoids (N × 6·25) . = ·3720 „ „
Acid as lactic acid = ·0517

1·7733

This subtracted from 2·0337 leaves ·2604 grms. of other organic matters. A portion of this consists in all probability of nitrogenous matter, as it is now well known that the factor 6·25 for calculating the nitrogen of malt into its corresponding albuminoid is far from correct, and is only used for want of a more accurate one. Another portion of this difference would no doubt consist of reducing sugars, this being greater or less according to the extent to which the proportion of these sugars in the malt differed from the standard set up. There is no doubt that certain other bodies are present in malt in addition to those already mentioned, about which nothing whatever is known at present. Perhaps a more correct method of arriving at the amount of the ready-formed sugars in malt would be by eliminating them by fermentation. This matter is at present under consideration.

Moritz and Morris (Science of Brewing, 472) arrive at the amount of ready-formed sugars by subtracting the sum of the albuminoids (derived from total nitrogen multiplied by 6·3), ash and lactic acid from the total solids obtained by dividing the sp.gr. of the cold mash, less 1000, by 3·86. But in the opinion of the writer much greater errors are introduced by this method than by the one given above.

The *moisture* is determined by drying the malt at first for twenty-four hours *in vacuo* over sulphuric acid, and then in a current of dry air at 100°C. until a constant weight is obtained. With the malt in question ·5 grms. gave ·1175 = 2·35 grms. p.c. The percentage of the various constituents are readily obtained by multiplying grms. per 100 c.c. by 10.

The complete analysis of the malt will then stand as follows:—

Dextrin		11·51
Maltose		36·96
Cane sugar		4·53
Other ready-formed sugars .		8·96
Unknown bodies . . .		2·60
Albuminoids (cold mash) .	3·72	3·95
Albuminoids (hot mash) .	0·23	
Acid as lactic acid . . .		·52
Ash		1·10
Moisture		2·35
Grains (insoluble matter) by diff.		24·52
Specific rotatory power of wort $[\alpha]_D$		114·3

From an analysis such as the above much useful information may be derived as to the character of the malt.

The cane sugar and the other ready-formed sugars are high, showing the grain to have been highly germinated. As a natural sequence to this the diastatic activity also is high, as shown by the comparatively low dextrin percentage as well as low specific rotatory power.

48. *Analysis of malt wort.* No very accurate process can be applied to the complete examination of malt wort; neither is it very necessary that such an examination should be made, for in the usual course of operations in a brewery the analysis of the various malts from which the wort is produced, as well as of the resulting beer, furnish a sufficient amount of information to the brewer as to the character of his wort, more especially if the mash in the laboratory is carried on at the same temperature, and under as similar conditions as it is possible to obtain for it, as the mash on the large scale in the brewery. There is, however, one point in connection with malt wort which is of some interest to the brewer, and that is its specific rotatory power, for from this may be derived, by inference, some knowledge as to the probable composition of his wort, anyway so far as the starch products are concerned. For it has been found by experience that a wort which polarises high prior to fermentation generally produces a highly dextrinous, full-flavoured beer, whilst the very opposite holds for a low polarising wort. In order to obtain an accurate idea of the polarimetric indications of malt wort, this must be submitted to polarisation after it has been boiled up with hops in the copper.

During the boiling a large proportion of the albuminoids has been precipitated, and the dextrin percentage will have been fixed, so that the wort at this stage affords a very good index as to the dextrin percentage of the beer produced from it.

Boiling with hops removes a portion of the albuminoids, whilst a small quantity of hop extract is added; at the same time a slight alteration occurs in the carbohydrates other than those derived from the starch, probably being the inversion of a part of the still unacted-on cane sugar by the acid of the wort at boiling temperature. But practically the actual composition of the starch products in the wort is unaltered by boiling with hops.

Where some form of glucose or saccharine is used in the brewing, it is obvious that for purposes of analysis the sample of wort must be taken from the copper before such sugar is added.

The sample, about one pint, is cooled down to 15·5°C., a drop or two of finings added, stirred up well, let lie 15 minutes or more, and filtered. The filtrate is generally bright, but too dark in colour for polarising. This may be got over by diluting to one-half, or one-fourth, with distilled water, or by decolourising by means of lead acetate and animal charcoal.

The tube is then filled with the decolourised wort, placed in the polariscope, and the deviation read off in angular degrees or divisions, as the case may be. At the same time the specific gravity of the wort is taken by means of the bottle, or by a gravimeter. The specific gravity −1,000 divided by 3·86 gives the number of grms. of solid matter per 100 c.c. of wort; the specific rotatory power may then be calculated by means of the formula—

$$[\alpha] = \frac{100\alpha}{2c}.$$

For instance, a sample of wort, sp.gr. = 1046·1, containing 11·943 grms. solid matter per 100 c.c., gave a rotation $\alpha_D = 28{\cdot}4$,

$$\text{therefore } [\alpha]_D = \frac{100\alpha}{2c} = \frac{100 \times 28{\cdot}4}{2 \times 11{\cdot}943} = 119{\cdot}0.$$

This is the specific rotatory power of this wort for ray D, or with the transition tint, using a Soleil-Ventzke-Scheibler instrument.

Deflection in 200 mm. tube = 82.

$$\alpha_j = 82 \times {\cdot}384 = 31{\cdot}488$$

$$\therefore [\alpha]_j = \frac{100 \times 31{\cdot}488}{2 \times 11{\cdot}943} = 131{\cdot}8.$$

This number, viewed in conjunction with other factors, is capable of throwing a great deal of light, not only upon the diastatic activity of the malt, but upon the behaviour of the fermentation as well as the composition of the finished beer. For instance, of two worts brewed under exactly similar conditions, but from different malts, it is found that one polarises higher than the other, whence it may reasonably be concluded that one of these worts contains more dextrin and less maltose than the other—that is to say, the malt from which it was brewed possesses less diastatic power than the other. For example, of two malts A gave $[\alpha]_D = 122{\cdot}7$; B, a later malt, gave $[\alpha]_D = 115{\cdot}0$. The beers (pale ales) from these malts, on being analysed just after racking, had the following composition calculated in p.c. on original wort matter:—

—	Matter fermented	Maltose	Dextrin	Undetermined	$[\alpha]_D$
A	53·7	15·0	20·7	10·6	122·7
B	65·1	12·4	12·1	10·4	115·0

It will be observed that B has a much lower specific rotatory power than A, consequently the beers from B will be less dextrinous than those from A. Analysis shows this to have been the case. During fermentation also, B, the one containing the more maltose, attenuated more rapidly than A and to a lower degree.

In order, therefore, to produce a beer from B as nearly similar as possible to A, the mashing temperature for B must be raised until the worts from copper polarise same as A, when it will be found that the resulting beers will partake more or less of the same character as those of A. Hence it will at once be perceived that by means of the polarimeter one has perfect control over mashing heats, and necessarily over the fermentations and the character of the finished beer.

This method of polarisation of wort may be considerably shortened if carried on systematically from day to day, or at stated intervals, by diluting the wort with water until the specific gravity is exactly 1040 as read off with a delicate saccharometer or gravimeter, adding a few drops of finings, filtering bright, polarising, and noting the reading. By this means the taking of the specific gravity with the bottle and calculation of $[\alpha]_D$ may be dispensed with altogether. The question naturally arises, What reading on the polarimeter ought a normal wort to give? This can only be answered satisfactorily by the brewer himself, as that class of beer which may be extremely popular in one part of the country may be just the reverse in another. No wort, however, ought to give a lower angle on the half-shadow polarimeter than 21° in the 200 mm. tube for a sp.gr. = 1040; this corresponds to 60·7 divisions on the transition tint instrument of Soleil-Ventzke-Scheibler.

Very dark-coloured beer worts, as well as the worts of porters and stouts, must be decolourised previous to polarisation. This is accomplished with bleaching solution. 50 c.c. of the sample are transferred to a 100 c.c. flask, and a sufficient quantity of bleaching solution added until the liquid is sufficiently decolourised, sulphurous acid added, and the flask made up to the containing mark with water. If much gas is disengaged during the process, so as to form a persistent froth, this may be got rid of by the addition of a few drops of ether. Since the liquid is diluted one-half, the reading must be doubled to get the correct angle.

49. *Analysis of beer.* In making an analysis of a sample of beer, it is advisable that the sample should be drawn from the cask shortly after time of racking, or, at any rate, before the secondary or cask fermentation has commenced.

The following determinations are usually made:

a. Original gravity.
b. Specific gravity.
c. Sugars fermented.

d. Maltose unfermented.
e. Dextrin unfermented.
f. Albuminoids.
g. Acid, free and volatile.
h. Ash.

Original gravity. By the term 'original gravity' is meant the specific gravity of the boiled hopped wort when collected in the fermenting vessel, for the levying of duty according to the Inland Revenue Act of 1880, and prior to fermentation by yeast.

When the wort is submitted to the action of yeast the carbohydrates other than those derived from starch are first of all attacked and split up into alcohol and carbonic acid, and afterwards the greater portion of the maltose derived from the transformation of starch during the process of mashing. The growth of the yeast removes a portion of the albuminoids and some of the fermentable sugar. So that there remains in the beer, when the first stage of the fermentation is over and it is fit to be racked off into casks, the alcohol derived from the splitting up of the fermentable sugars by the action of yeast, as well as a portion of carbonic acid, the whole of the dextrin, a considerable portion of the maltose and of the albuminoids, hop matter, and other bodies generally classed as undetermined (Valentine, Jour. Soc. of Arts, 24, 404).

The following analyses of malt wort at various stages will show the changes which take place: –

TABLE XII.

100 parts by measure contain	Unboiled wort	After boiling with hops	Finished beer
Maltose	6·66	6·66	1·52
Dextrin	3·44	3·44	3·44
Other carbohydrates (ready-formed sugars of malt)	4·78	4·80	1·00
Albuminoids	1·45	1·05	0·66
Hop extract	–	0·33	0·33
Ash	0·17	0·27	0·24
Non-volatile products of fermentation	—	—	0·47
Total	16·50	16·55	7·66
Alcohol, sp.gr. 992	—	– –	4·18

It will be seen from the above that slightly less than 50 p.c. of the solid matter has disappeared during fermentation. The disappearance of this solid matter represents the loss of so many degrees of gravity, and will correspond approximately to the production of an equivalent amount of alcohol and carbonic acid. It is therefore possible by experiment to find the amount of solid matter which has disappeared during fermentation, and corresponding to a given quantity of alcohol present in the finished beer, and hence the number of degrees of gravity lost, so that by adding the number to the specific gravity of the residue left after distilling off the alcohol from a given bulk of beer and making up with distilled water to the original volume, it is possible to arrive at the specific gravity of the wort prior to fermentation, *i.e.* the original gravity of the beer. A very elaborate series of experiments with this object in view has been carried out, and the methods of determining the original gravities of beer worts have been very carefully investigated by Graham, Hofman, and Redwood (Report on Original Gravities, 1852).

The method usually adopted, as the result of their experiments, for determining the original gravity of beer is as follows:

A given measure of the beer, generally 100 c.c., is taken at normal temperature (15·5°C.) and transferred to a distilling flask, the measuring flask being well rinsed out with distilled water and the rinsings added to the beer in the distilling flask, which is then connected with a good condenser and the beer distilled. The distillate is collected in a 100 c.c. flask. When the distillate has reached nearly to the neck of the flask, the distillation is stopped, the distillate cooled down to 15·5°C., made up with distilled water to the containing mark, shaken well up, and its specific gravity taken in the usual manner. The residue in the distilling flask is allowed to cool, transferred to a 100 c.c. flask, the distilling flask being rinsed out with a little distilled water two or three times and added to the residue, which is then made up to the containing mark with distilled water at 15·5°C. and its specific gravity determined. From the numbers thus obtained the original gravity is calculated as follows:

The specific gravity of the distillate subtracted from 1,000 gives what is called the 'spirit indication,' and from this, by means of a table constructed for the purpose, may be found the number of degrees of gravity lost during fermentation, whence may be obtained the original gravity of the beer by adding this number to the specific gravity of the residue.

Table XIII. has been constructed on the assumption that during fermentation certain acids, equivalent to one part of acid in 1,000 measures of beer, are produced, and which for convenience are all reckoned as acetic acid, so that in determining the original gravity of beers containing about this amount no correction for acid is necessary. But when a beer has become very acid through age or other causes a certain allowance must be made for the acid contained in it, since the acid has been formed at the expense of an equivalent quantity of alcohol, and during distillation that portion of the acid which is volatile (acetic acid) will distil over with the alcohol, and give rise to errors in the determination of the original gravity. It becomes necessary, therefore, to neutralise the acid before

TABLE XIII. *Spirit indication with corresponding degrees of gravity lost in malt worts by the 'Distillation Process.'*

	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	33·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	71·1	71·7	72·3	72·9	73·5	74·1	74·4	75·3	75·9

distillation. This is best done by adding enough carbonate of soda to render the beer very slightly alkaline.

The total acidity must be determined in a fresh portion of beer, 100 c.c. being taken for the purpose, and titrated with $\frac{n}{2}$ ammonia solution, using neutral litmus paper as an indicator. The percentage of total acid in the beer having been determined, the necessary correction is made for it by reference to a table for corresponding loss of spirit indication, and the number so found is added to the spirit indication deduced from the alcohol obtained by distillation.

TABLE XIV. *For ascertaining the value of the acetic acid.*

Excess p.c. of the acetic acid in the beer	Corresponding degrees of spirit indication									
—	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·0	—	·02	·04	·06	·07	·08	·09	·11	·12	·13
·1	·14	·15	·17	·18	·19	·21	·22	·23	·24	·26
·2	·27	·28	·29	·31	·32	·33	·34	·35	·37	·38
·3	·39	·40	·42	·43	·44	·46	·47	·48	·49	·51
·4	·52	·53	·55	·56	·57	·59	·60	·61	·62	·64
·5	·65	·66	·67	·69	·70	·71	·72	·73	·75	·76
·6	·77	·78	·80	·81	·82	·84	·85	·86	·87	·89
·7	·90	·91	·93	·94	·95	·97	·98	·99	1·00	1·02
·8	1·03	1·04	1·05	1·07	1·08	1·09	1·10	1·11	1·13	1·14
·9	1·15	1·16	1·18	1·19	1·21	1·22	1·23	1·25	1·26	1·28
1·0	1·29	1·31	1·33	1·35	1·35	1·37	1·38	1·40	1·41	1·42

The following estimation of the original gravity of beer which had gone decidedly acid serves as an example:

Extractive . . . . . = 1013·30
Distillate . . . 990·15
Spirit indication . . 9·85
Spirit indication derived from acid . . . = ·93
Total spirit indication = 10·78
Equivalent degrees of gravity = 47·90
Original gravity = 1061·20

Total acid 100 c.c. required 24 c.c. $\frac{n}{2}$ ammonia.
= 0·72 grms. acetic acid per 100 c.c.
= ·93 spirit indication.

In order to obtain the respective amounts of volatile and free acid, 100 c.c. of beer are evaporated to dryness on the water-bath, the residue dissolved in water, and titrated with $\frac{n}{2}$ ammonia. This gives the fixed acid, which, deducted from the total acid, leaves the volatile acid. The fixed acid is usually calculated as lactic, and the volatile as acetic, acid. In the example already referred to, 100 c.c. of the beer after evaporation required 8 c.c. $\frac{n}{2}$ ammonia

= 0·36 grms. lactic acid per 100 c.c.
Volatile acid = ammonia required for total acid less ammonia required for fixed acid
= 24 c.c. – 8 c.c. = 16 c.c. = 0·48 grms. acetic acid per 100 c.c.

The optical activity in 200 mm. tube and cupric oxide reduction in grms. per 100 c.c. are next determined, and from these may be calculated the amount of unfermented maltose and dextrin in the residue.

The albuminoids and ash are determined as for malt wort.

The following analysis of a pale ale will illustrate the method:

Original gravity.

Sp.gr. of residue . . = 1024·85
Sp.gr. of distillate . . = 991·4

1000 − 991·4 = 8·6 spirit indication,

and from Table XIII. this corresponds to 37·0° of gravity lost during fermentation. This, added to the sp.gr. of the residue, gives the original gravity or the sp.gr. of the wort from which this beer was produced prior to fermentation.

1024·85 + 37·0 = 1061·85.

37·0 ÷ 3·86 = 9·5855 grms. per 100 c.c. of matter fermented.

Optical activity in 200 mm. tube = 13·4.

Cupric oxide reduction in grms. per 100 c.c. = 2·55.

From these data may be calculated the relative amounts of unfermented dextrin and maltose in the residue. The CuO, being entirely derived from the maltose, is multiplied by ·743, which gives the maltose present in grms. per 100 c.c. 2·25 × ·743 = 1·8946 grms. maltose; 1·8946 × 2·708 = 5·13 optical activity per 100 c.c. due to maltose; 13·4 − 5·13 = optical activity due to dextrin = 8·27, which divided by 3·9 = 2·1205 grms. dextrin per 100 c.c.

The number of degrees of gravity lost, divided by 3·86, gives the number of grms. of solid matter per 100 c.c. which have disappeared during fermentation.

Total Nitrogen, 10 c.c. of beer gave ·009 grms. = ·09 grms. per 100 c.c.

Ash, 50 c.c. of beer gave ·2027 = ·4054 grms. per 100 c.c.

The sum of the unfermented maltose, dextrin, albuminoids, and fixed acid subtracted from the total organic solids leaves the matters undetermined, consisting of hop extract, colouring matter, glycerine, and other products of fermentation, &c., thus:

Sp.gr. . . . . 1024·85
Correction for ash, ·4054 × 8 . . . = 3·24

1021·61 − 1000 ÷ 3·86 = 5·6000 grms. organic solids per 100 c.c.

Maltose (unfermented) in grms. per 100 c.c.	1·8946
Dextrin in grms. per 100 c.c. . .	2·1205
Albuminoids (N × 6·25) . . .	0·5625
	4·5776

This subtracted from 5·6000 leaves 1·0224 grms. undetermined matters.

The complete analysis expressed in grms. per 100 c.c. stands thus:

Maltose (unfermented) .	1·8946
Dextrin	2·1205
Albuminoids	0·5625
Undetermined	1·0224
Ash	0·4054
Total solid matters .	6·0054

It is usual to state these results as percentages on the total solid matters contained in the original wort. In this case the original gravity of the beer was found to be 1061·85; this corrected for ash, 1061·85 − 3·24 = 1058·61, which, less 1000 and divided by 3·86, gives 15·1839 grms. organic solid matters per 100 c.c. Adding the ash to this, the total solid matters per 100 c.c. present in the wort before fermentation are found to be 15·5893 grms.

Therefore, multiplying each of the constituents of the extractive by 100, and dividing by 15·5893, the results of analysis calculated as percentages on the original wort solids are obtained.

Matter (fermented) . . .	61·48
Maltose (unfermented) . .	12·15
Dextrin	13·60
Albuminoids (N × 6·25) . .	3·61
Undetermined organic matters .	6·56
Ash	2·60
Total	100·00

50. Perhaps this part of the article on wort and beer analysis would hardly be complete without referring to the existence of the so-called amyloïns or maltodextrins in malt wort and beer.

According to Brown and Morris (Trans. Lab. Club, 3, 81), a normal beer, when racked, contains little or no free maltose, the apparent maltose in the beer existing for the most part as maltodextrins, which require to be degraded before they become fermentable. On storage, degradation gradually takes place under the influence of the secondary yeast forms; free maltose is produced, and fermentation starts once more.

The following methods for the estimation of these bodies in malt, in wort, and in beer are given by Moritz and Morris (Science of Brewing, p. 477, 481, 504).

The principles of the methods to be employed are these: first, the free maltose and other fermentable sugars are fermented away; the reducing sugar remaining after fermentation will then be due to maltose, locked up as maltodextrin, and to certain other substances, partly caramelisation products, and partly salts of organic acids, which are unfermentable and unaffected by diastase. A correction is made for these substances. The wort is then degraded with a diastase solution (cold-water malt extract), by means of which the whole of the maltodextrins become converted into maltose. The increase in the amount of maltose so produced will then give, on calculation, the amount of dextrin originally locked up as maltodextrin. This, added to the maltose previously found as maltodextrin, gives the total amount, and the ratio of one to the other will give the type of maltodextrin.

[illegible] *trins.* 50 c.c. of the hot-water mash (prepared as before described) are 'pitched' with 0·25 grm. yeast, and the fermentation allowed to proceed at 80° F. for 72 hours. The mixture is then made up to 200 c.c. and filtered bright; 25 c.c. of the filtrate are now taken for the determination of the cupric reducing power. In order to arrive at a suitable correction for the reducing bodies previously mentioned, another 50 c.c. of the hot-water mash are set to ferment with the same amount of yeast, to which is added 0·25 c.c. of a normal cold-water malt extract. The conditions of fermentation are precisely the same as before described. At the expiration of the fermentation the mixture is made up to 200 c.c., filtered bright, and 25 c.c.

of the filtrate taken for the determination of the cupric reducing action. The cold-water malt extract will convert the whole of the maltodextrins into maltose, which will ferment away during the process of fermentation. The reducing action in this case will therefore be entirely due to the reducing substances previously referred to, and if this reduction be subtracted from that obtained in the case of the first fermentation the difference will be due to the combined maltose only.

Example. 50 c.c. of the hot-water mash were fermented as above, and 25 c.c. fermented fluid gave 0·032 grms. CuO; 50 c.c. of the same mash were similarly fermented with the cold-water extract, and 25 c.c. of the fermented liquid gave 0·010 grm. CuO. The reduction due to combined maltose is therefore 0·032 − 0·10 = 0·022 grm. CuO. This calculated into the corresponding amount of maltose (by multiplying by 0·743) gives the figures 0·016346 maltose in 25 c.c.; or in 100 c.c., 0·0732. This is the amount in 100 c.c. of the diluted solution (50 c.c. diluted to 200 c.c.). Therefore, in 100 c.c. of the original hot-water mash the amount of maltose in the maltodextrins would be 0·0732 × 4 = 0·29 grm. On the malt, therefore, the percentage of combined maltose is 2·90.

(*b*) *Determination of Dextrin in Maltodextrins.* 25 c.c. of the hot-water mash are taken, and 2·5 c.c. of normal cold-water extract are added. The whole is digested for one hour at 130°F., then cooled, diluted to 100 c.c., and 10 c.c. taken for the determination of the cupric reducing action. The reducing action of 1 c.c. of the cold-water extract is taken, after first diluting to about 10 c.c., and then digesting for one hour at 130°F.

Example. The total reducing action of the hot-water mash from a given sample of malt was 0·292 grm. CuO per 5 c.c.; or on 100 c.c., 5·84 grms. CuO.

In the above determination of dextrin in maltodextrin 10 c.c. of the hot-water mash, after degradation and dilution, gave 0·17 grm. CuO. From this may be at once subtracted the CuO due to the malt extract used. By a preparatory determination 1 c.c. is found to yield 0·08 grm. CuO, and the 10 c.c. of hot-water mash used above will contain one-fourth of this, or 0·02. After correction for the cold extract, 10 c.c. will therefore give 0·17 − 0·02 = 0·15; 100 c.c. of the diluted extract will therefore give 1·5 grms. This corresponds to 25 c.c. of original wort; 100 c.c. of original wort will therefore give 6·0 grms. CuO.

Now the same amount of original wort previous to degradation gave 5·84; the increase due to degradation of combined dextrin is, therefore, 0·16. This is calculated into dextrin by multiplying by the factor 0·706, 0·16 × 0·706 = 0·11 grm. To calculate this on 100 parts malt, multiply by 10. The malt therefore yields 1·10 p.c. of dextrin as maltodextrin. It has been previously found that the combined maltose on 100 parts malt is 2·90; the combined dextrin is 1·10. The total maltodextrin is therefore 4·00 p.c. From the previous analysis the total maltose was found to be 31·35 p.c. Of this, 2·90 is combined; the balance (28·45) will be free. The total dextrin was 13·44. 1·10 of this is combined; the balance (12·34) will be free, or stable, dextrin. The full results will therefore be (on 100 parts of malt):

Maltose (free)		28·45 p.c.
Dextrin (free)		12·34 „
Maltodextrins	$\left\{\begin{array}{l}2\cdot90 \text{ maltose}\\ 1\cdot10 \text{ dextrin}\end{array}\right\}$	4·00 „

These figures are generally calculated and stated on 100 parts of solid matter in the wort, so as to exclude the various factors of moisture and grains. In this case the wort solids were 65·64 p.c. The required result may be obtained by multiplying the previous figures by 100 and dividing by 65·64. The free maltose, free dextrin, and maltodextrins will therefore in this case be—

Maltose (free)		43·19 p.c.
Dextrin (free)		18·80 „
Maltodextrins	$\left\{\begin{array}{l}4\cdot42 \text{ maltose}\\ 1\cdot68 \text{ dextrin}\end{array}\right\}$	6·10 „

It will be noted that the maltodextrins produced from the sample of malt under the mashing conditions adopted approximate closely to the $\left\{\begin{array}{l}3M\\ 1D\end{array}\right\}$ type.

Preparation of Normal Malt Extract. 400 grms. of ground pale malt are mixed with a litre of distilled water, to which 5 c.c. of chloroform have been added. The malt is allowed to soak for 48 hours. The malt is then strained off, and the solution filtered bright. The chloroform preserves the solution from decomposition for about a fortnight. When no chloroform is used it has to be made fresh each time, and this necessitates determining afresh the necessary correction for the reducing power due to the carbohydrates dissolved in cold water. Preserved with chloroform, the same corrections apply until the solution becomes turbid. Directly turbidity makes its appearance another solution must be prepared, and the correction again determined. The mode of determining the correction for the reducing sugars in the solution has been given.

Determination of Maltodextrins in Wort.

(*a*) *Determination of Combined Dextrin.* 2 c.c. of wort are taken for the total cupric reducing action. Amount of CuO yielded, 0·30 grm.

20 c.c. of the wort are now digested with 2·5 c.c. of normal cold water extract for one hour at 130°F. The mixture is then cooled, diluted to 100 c.c., and 10 c.c. of the diluted liquid taken for the determination of the reducing power. This amount of degraded and diluted wort gave 0·34 grm. CuO. From this must be subtracted the correction for cupric reducing action of cold extract (1 c.c. = 0·08 grm. CuO).

From 0·34 is therefore subtracted 0·02, giving 0·32. The CuO on the same quantity of original wort (2 c.c.) was 0·30. The increase is, therefore, 0·02, due to degradation of combined dextrin on 100 c.c.; the increase will be 0·02 × 50 = 1·00 grm. CuO equivalent to combined dextrin 1·00 × 0·706 = 0·706 grm.

(*b*) *Determination of Combined Maltose.* 50 c.c. of the wort are 'pitched' with 0·25 grm. yeast; another 5 c.c. treated in the same way with yeast, and 0·25 c.c. malt extract added.

Both worts are fermented in the manner previously described. After fermentation, both are diluted to 200 c.c., filtered, and 25 c.c. of each taken for the determination of cupric reducing action.

Reducing action of wort without diastase on above quantity, 0·13 grm. CuO. Reducing action of wort with diastase, 0·07 grm. CuO. Reduction due to combined maltose, 0·06 grm. CuO.

To calculate this on 100 c.c. of original wort, 0·06 is multiplied by 16; CuO from 100 c.c. of original wort will, therefore, be 0·96 grm. CuO. The combined maltose will therefore be (on 100 c.c. wort) 0·96 × 0·743 = 0·71 grm. The combined maltose and the combined dextrin in 100 c.c. of wort are now known; to calculate these on the wort solids, the results are multiplied by 100, and divided by the solid matter per 100 c.c. (16·24 grms.). Combined maltose on 100 parts of wort solids will therefore be $0·71 \times \frac{100}{16·24}$, and the combined dextrin $0·706 \times \frac{100}{16·24}$.

The results, therefore, stand (on 100 parts of wort solids):

Maltose in maltodextrins . .	4·37
Dextrin in maltodextrins . .	4·34
Total maltodextrins . .	8·71
Type . . .	1 M 1 D

Determination of Maltodextrin; Dextrin; Fermented Sugars; and Fermentable low type Maltodextrins (apparent free Maltose) unfermented in Beer. For this the following estimations are required.

Total cupric reducing power. Take 5 c.c. (2 to 3 c.c. for very strong beers and 10 c.c. for very weak beers) and determine cupric reducing power on Fehling's solution in the usual way.

Opticity. 50 c.c. of the beer are taken, a little alumina added, the whole diluted to 100 c.c., filtered, and the opticity determined in the usual way in a 100 mm. tube.

Degradation by malt extract. 50 c.c. of beer are evaporated to about half its bulk, and transferred to 100 c.c. measuring flask, 5 c.c. of cold water extract (normal strength) added, and the whole digested at 125 F. for one hour. It is then cooled, diluted to 100 c.c., and the reducing power determined in 10 c.c.

The cupric reducing power of the cold water malt extract is estimated in 1 c.c., and the figure thus obtained is applied as a correction.

Fermentation. 50 c.c. of the beer are evaporated to about 25 c.c., diluted to about 100 c.c. with cold water, and about 0·25 grm. yeast added. Ferment for 72 hours at 80 F.; then add some alumina, dilute to 200 c.c., filter, and estimate the cupric reducing power in 25 c.c. of filtrate.

To correct the above for the non-degradable, unfermentable, reducing substances present in beer, a duplicate of the above is fermented in precisely the same manner, the only difference being the addition, prior to fermentation, of 0·25 c.c. of cold-water malt extract. The cupric reducing action is, as before, taken in 25 c.c., after dilution to 200 c.c., and filtration.

Example:

Original gravity . . .	1074·75
Specific gravity . . .	1021·38

Cupric reducing power. 2 c.c. taken; CuO obtained, 0·083 grm. The above is calculated into total maltose on 100 c.c. of beer: 0·083 × 0·743 × 50 = 3·08 grms. maltose.

Opticity. 50 c.c. of the beer diluted to 100 c.c.; reading in 100 mm. tube = 12·4 divs. To get the dextrin, the reading must be doubled to correct for previous dilution:

$$12·4 \times 2 = 24·8.$$

Reading due to maltose will be 3·08 × 3·905 = 12·01 divs.

Reading due to dextrin will be 24·8 − 12·01 = 12·79 divs.

$$\text{Per cent. of dextrin in beer } \frac{12·79}{5·625} = 2·27.$$

Degradation. 50 c.c. of beer are taken, and 5 c.c. of cold extract used; the whole after degradation diluted to 100 c.c.: CuO from 10 c.c. = 0·2985 grm. The CuO per 1 c.c. of cold-water extract was found to be 0·08 grm. Before correcting, the total maltose after degradation in 100 c.c. of the degraded mixture must be calculated thus:

$$0·2985 \times 0·743 \times \frac{100}{10} = 2·216 \text{ grms. maltose.}$$

This is corrected for the CuO given by the malt extract as follows:—

$$0·08 \times 5 \times 0·743 = 0·297 \text{ grms. maltose.}$$

Then 2·216 less 0·297 = 1·919 = maltose after degradation in 100 c.c of the degraded mixture; or, in 100 c.c. beer $1·919 \times \frac{100}{50} = 3·838$ grms. maltose.

The above figures represent total maltose plus the maltose formed by degradation of the combined (or amyloïn) dextrin. Combined or amyloïn dextrin is therefore 3·838, less total maltose 3·08, after deducting the increase in molecular weight due to conversion into maltose; thus: 3·838 − 3·08 = 0·758, and 0·758 × 0·95 = 0·72 grm. combined dextrin in 100 c.c. of beer.

Fermentation. (*a*) Without malt extract: 50 c.c. taken; after fermentation and dilution to 200 c.c., 25 c.c. taken for reducing action gave 0·171 grm. CuO. (*b*) With malt extract: the same quantities gave 0·12 grm. CuO.

CuO due to combined maltose 0·174-0·12 = 0·054; $0·054 \times 0·743 \times \frac{200}{25} \times \frac{100}{50} = 0·64$ grm. combined maltose (amyloïn maltose) in 100 c.c. of beer.

The apparent free maltose can now be calculated *i.e.* the low type maltodextrins unfermented during brewery fermentation, but fermented during the laboratory fermentation. To do this, the maltose unfermented during fermentation without malt extract is subtracted from the total maltose; the latter figure will be $0·171 \times 0·743 \times \frac{200}{25} \times \frac{100}{50} = 2·07.$

Total maltose . . .	3·08 grms.
Maltose after fermentation .	2·07 ,,
Fermentable maltodextrins calculated as maltose .	1·01 ,,

The free dextrin will be the difference between the total dextrin and combined dextrin —*i.e.* 2·27 less 0·72 = 1·55.

The ash and albuminoids and mixed acid in this beer, calculated on 100 parts of the wort solids, were respectively

Ash	1·34 p.c.
Albuminoids	3·36 ,,
Acid as lactic acid	0·52 ,,

The following will represent the analysis calculated on 100 parts of original wort solids.

	On 100 parts original wort solids	
Maltose and other fermentable sugars fermented during brewing fermentation	58·47	
Low type maltodextrins unfermented during brewery fermentation, but fermentable with active yeast (so-called free maltose)	5·22	
Maltose in maltodextrins	3·30	*
Dextrin in maltodextrins	3·72	
Free dextrin	8·01	
Mineral matter	1·34	
Nitrogenous matter as albuminoids	3·36	
Acid as lactic acid	0·52	
Undetermined matter (hop-extract, glycerine, unfermentable portions of malt adjuncts, and malt worts, &c. &c.), by difference	16·06	
	100·00	

* Total maltodextrins = 7·02.

Original gravity	1074·75
Specific gravity	1021·38
Free acid in 100 c.c. of beer (acetic acid)	0 05
Fixed acid as lactic acid	0·15

51. *Estimation of Lactose* (*milk sugar*). The estimation of lactose is in technical analysis only required in the examination of milk and milk products. This is best accomplished by means of the polarimeter, but before this method can be applied certain albumens which are always present in milk, and which possess a left-handed rotation, must be removed as well as the fat. The most reliable method for insuring this appears to be that recommended by Wiley (A. 6, 289), which is as follows:

The sp.gr. of the milk is first determined; if this should be 1026 (water = 1000) or thereabouts, 60·5 c.c. of the milk are transferred to a 100 c.c. flask and 1 c.c. of mercuric nitrate solution, or 30 c.c. of mercuric iodide solution, (preferably the latter), added. The liquid in the flask is then made up to 102·4 c.c. with distilled water, well shaken up, filtered bright, and polarised in the 200 mm. tube.

The volume is made up to 102·4 c.c. because the precipitated albumen occupies a volume of about 2·4 c.c., so that the solution is really diluted to 100 c.c. Should the sp.gr. of the milk be 1030, 60 c.c. are taken instead of 60·5 c.c., and if the sp.gr. be 1034, 59·5 c.c. are taken.

The room and milk should be at one constant temperature, and the polarisation taken at the same, about 20°C. being the best suited for the purpose, although a few degrees above or below will not appreciably affect the results.

In the above method the specific rotatory power of lactose for ray D is taken to be 52·5, and the weight of it in 100 c.c. solution required to read 100 divisions on the cane sugar scale to be 20·56 grms. This is the weight necessary to be taken for instruments requiring 16·19 grms. of cane sugar to produce a rotation equal to 100 divisions.

It will, however, be easy to calculate the number for milk sugar whatever instrument is employed. Thus for the Ventzke-Scheibler instrument, since the weight of cane sugar in 100 c.c. required to read off 100 divisions is 26·048 grms., therefore

$26{\cdot}048 : x = 58{\cdot}2$ (α_j of lactose) : $73{\cdot}8$ (α_j cane sugar),

whence $x = 33{\cdot}03$ grms.; hence 1 division of this scale = ·3303 grms. lactose.

The mercuric solutions are prepared as follows: Mercuric nitrate by dissolving mercury in double its weight of nitric acid (sp.gr. 1·42), then adding to the solution an equal volume of water. 1 c.c. of this reagent is sufficient to precipitate the albumen in 50 to 60 c.c. of milk.

Mercuric iodide solution

Potassium iodide	33·2 grms.
Mercuric chloride	13·5 ,,
Acetic acid (sp.gr. 1·040)	20·0 c.c.
Water	640 ,,

30 c.c. of this solution are required for 50–60 c.c. milk.

So far it will be seen that the polarimeter has only been applied to the detection and estimation of the different carbohydrates as they occur in various commercial products, but in addition to the carbohydrates and their derivatives, other widely differing substances also possess the power of rotating a ray of polarised light. Such are a large number of the vegetable alkaloids and acids, essential oils, terpenes, resins, camphors, bile constituents, albumens, &c. Reliable data as to the optical properties of several of these bodies have been obtained, which are extremely useful in determining the nature of such substances as well as in examining the purity of particular samples, and in many cases of detecting adulteration with other bodies, whether they be inactive or active. The following examples will serve to illustrate the wide field covered by polarimetric observations—a field which is widening more and more every year, as additional information is obtained on one of the most interesting methods of chemical analysis and scientific investigation.

52. *Cinchona alkaloids.* Although a direct estimation of the alkaloids in cinchona bark extract cannot be made with anything like accuracy by means of the polarimeter, nevertheless a useful check on the results obtained by other modes of analysis is provided by means of it. It can, however, be made to serve a most useful purpose in testing the relative purity of commercial samples of the several alkaloids. The specific rotatory power of these alkaloids, and of their most important salts, has been studied in detail by Hesse (Ann. 176, 203; 182, 128) and Oudemans (Ann. 188, 33), the results of whose researches are given very con-

cisely and clearly by Landolt in his Handbook, p. 198, and of which only a very brief abstract can be given here.

The constants given by Hesse and Oudemans serve for testing the purity of commercial samples. For this it is necessary, of course, that the conditions in respect of solvent and concentration should be the same as in the determination of these normal values, and the temperature should not differ very much. Moreover, it is necessary in dealing with compounds containing water of crystallisation to determine directly the amount of the latter, in order to establish the identity of the same with the formula assigned, or, if it disagrees, to be able to find the percentage of anhydrous substance—viz. of alkaloid present.

The differences which occur when impurities are present are much larger in amount when another alkaloid is present, the specific rotation of the four cinchona bases differing very considerably from one another. This is shown in a number of experiments by Hesse, of which the results are as follows:—A solution of a specimen of neutral diquinine sulphate, which a separate analysis showed to contain 15 p.c. of water of crystallisation, was prepared with hydrochloric acid, having a concentration $c = 2$ grms. anhydrous base. To prepare 50 c.c. of this solution, since 85 parts of anhydrous base were equivalent to 100 parts of the hydrated substances,

$$\frac{1 \times 100}{85} = 1{\cdot}176 \text{ grms.}$$

was required. This amount was put in a 50 c.c. flask, together with so much standard hydrochloric acid to give for one molecule $(C_{20}H_{24}N_2O_2)_2.H_2SO_4$ four molecules HCl, and the resulting solution diluted up to the mark with water. Observed in a Wild's polariscope with a 200 mm. tube, the solution gave an angle of rotation $\alpha_D = -9{\cdot}58°$, whence the specific rotation of the anhydrous substance

$$[\alpha]_D = -\frac{9{\cdot}58 \times 100}{2 \times 2} = -239{\cdot}5°.$$

Now, the figures in Table VII. show that perfectly pure sulphate of quinine in such a solution gives $[\alpha]^D = -239{\cdot}2°$; and hence the preparation under examination must have been free from admixture. Three other samples of commercial sulphate of quinine, examined under like conditions, gave the following specific rotations respectively:

$$-236{\cdot}6°;\ -235{\cdot}5°;\ -109{\cdot}5°.$$

Of these the two first agree so nearly with the normal value that no admixture of foreign substance, at least in any appreciable quantity, could have been present. The third, on the contrary, shows such a marked rotation to the right that it must contain a notable amount of quinidine and cinchonine.

Optical analysis of mixtures of cinchona alkaloids. The quantitative composition of a mixture of two alkaloids may be deduced from its specific rotation with the aid of the values given in Table VII.

To test this method, Hesse determined the specific rotations of a number of mixtures of known composition to ascertain whether the former could be deduced from the rotatory powers of the constituents. This was found to be sufficiently exact, and therefore the association of alkaloids in solution does not materially interfere with their individual optical properties. Hence a quantitative analysis by this method is practicable. The mode in which the percentage composition of a mixture of two alkaloids is deduced from the observation of its specific rotation will be seen from the following examples given by Hesse:—

1. Four grms. of a mixture of quinine hydrate and cinchonidine were dissolved in alcohol of 97 p.c. by volume to form 100 c.c. of solution. Examined in Wild's polariscope with a 200 mm. tube, the solution gave an angle of rotation $\alpha_D = -9{\cdot}95°$, and thus the specific rotation of the mixture was

$$[\alpha]_D = -\frac{9{\cdot}95 \times 100}{2 \times 4} = -124{\cdot}37°.$$

The specific rotation of the individual alkaloids is, according to Table VII., when $c = 4$,

Quinine hydrate, $[\alpha]_D = -142{\cdot}57°$.
Cinchonidine, $[\alpha]^D = -106{\cdot}29°$.

Putting x for the required percentage of quinine hydrate, whereby that of cinchonidine $= 100 - x$, the following equation is obtained.

$$-142{\cdot}57x - 106{\cdot}29(100 - x) = 124{\cdot}37 \times 100,$$

whence

$$x = \frac{100(124{\cdot}37 - 106{\cdot}29)}{124{\cdot}57 - 106{\cdot}29}.$$

According to this the mixture consists of—

Quinine hydrate	. .	49·8 parts
Cinchonidine	. . .	50·2 „
		100·0

The real composition of the mixture actually consisted of equal parts of the alkaloids, with which the results of optical analysis coincide almost exactly.

2. A mixture of 3 parts quinine sulphate and 1 part quinidine sulphate gave, in an aqueous solution containing 4 grms. in 100 c.c., the specific rotation $[\alpha]_D = -71{\cdot}87°$:

For quinine sulphate according to Table VII. when $c = 4$:

$$[\alpha]_D = -163{\cdot}61°.$$

For quinidine sulphate according to Table VII. when $c = 4$:

$$[\alpha]_D = +208{\cdot}80°.$$

Indicating by x the percentage of quinine sulphate the equation $-163{\cdot}61x + 208{\cdot}80(100 - x) = 71{\cdot}87 \times 100$ is obtained; whence $x = 75{\cdot}4$ p.c.

Whence—

		[illegible]	[illegible]
Quinine sulphate	.	75·4	75·0
Quinidine sulphate	.	24·6	25·0
		100·0	100·0

53. *Oil of turpentine.* Three varieties of oil of turpentine are known in commerce, French, Russian, and American, and these differ in a very marked degree in their action on polarised light, for whereas the French variety is lævorotatory, both the Russian and American are dextrorotatory.

For French turpentine, Armstrong (S. C. I. 1, 478) finds the value of $[\alpha]_D$, using a 200 mm. tube, to be on the average -60 to $-61°$, whilst American turpentine under similar conditions v[illegible] from $+30°$ to $+45°$.

Commercially, Russian turpentine is not of much importance, being unsuitable for the purposes to which the other two are applied, but since it is much cheaper than either of these it is sometimes added to them as an adulterant.

Other adulterants of oil of turpentine are petroleum and shale spirit, coal-tar naphtha, resin oil, and resin spirit. In the detection of adulteration, determination of the specific rotatory power alone, although not conclusive in the case of adulteration of American oil of turpentine, nevertheless serves as a useful indicator. In the case of French oil of turpentine, on the other hand, where nothing like so great deviation from the average is shown in the polarisation of various samples, the addition of adulterants may be readily detected with a fair approximation to accuracy. According to Aignan (C. R. 109, 944), French turpentine is frequently adulterated by the addition of resin oils, though only to the extent of about 5 p.c., the addition of these oils causing a decrease in the lævorotatory power of the turpentine oil.

Aignan finds that the white oils which are obtained by distilling colophony and further rectification may be divided into three groups, possessing the following respective rotatory powers: $[\alpha]_D = -72°, -32°, -21°$. The first of these is the one generally used for the adulteration of the turpentine, and although it has a higher specific rotatory power of the same sign, the rotatory power of the mixture is lower than the normal rotatory power of the oil of turpentine. These different qualities were mixed with oil of turpentine and polarised, from which he deduced the following results:—

Mixture with oil of first quality,

$$[\alpha]_D = -61{\cdot}5° + \frac{7{\cdot}5}{5}h.$$

Mixture with oil of second quality,

$$[\alpha]_D = -61{\cdot}5° + \frac{8{\cdot}5}{5}h.$$

Mixture with oil of third quality,

$$[\alpha]_D = -61{\cdot}5° + \frac{5{\cdot}5}{5}h.$$

Where h = percentage of resinous oils contained in the mixture.

Detection of oil of turpentine as an adulterant in essence of lemon. French oil of turpentine is sometimes used to adulterate essence of lemon, and owing to the percentage composition of the two oils being identical, and their boiling-points and densities being almost the same, the presence of the adulterant is difficult to detect. Oliveri (Gazzetta, 21, 318) finds that the readiest method of detecting the fraud is by observing the specific rotatory power of the sample, as French oil of turpentine has a lævorotatory power of −55° in 200 mm. tube, whilst oil of lemon rotates the polarised ray, under similar conditions, about 120° to the right. Its presence is at once detected, and may easily be calculated, as the rotatory power of the mixture is the algebraic sum of the rotatory powers of its constituents taken in the proportions in which they are present.

The percentage of the adulterant may be obtained by means of the following table, from the specific rotatory power of the sample taken in a 200 mm. tube:—

Table for detection of adulteration of essence of lemon with oil of turpentine.

Adulterated with p.c. of oil of turpentine	Rotation in 200 mm. tube	Adulterated with p.c. of oil of turpentine	Rotation in 200 mm. tube
0 p.c.	120·00	11 p.c.	100·75
1 ,,	118·25	12 ,,	99·00
2 ,,	116·50	13 ,,	97·25
3 ,,	114·75	14 ,,	95·50
4 ,,	113·00	15 ,,	93·75
5 ,,	111·25	16 ,,	92·00
6 ,,	109·50	17 ,,	90·25
7 ,,	107·75	18 ,,	88·50
8 ,,	106·00	19 ,,	86·75
9 ,,	104·25	20 ,,	85·00
10 ,,	102·50		

54. *Vegetable Oils.* Linseed oil is frequently adulterated with resin oil, and as the former possesses no rotatory power and the latter does, the amount of adulteration may be determined in a mixture of the two oils by means of the polarimeter (Aignan, C. R. 110, 1273). The rotation is +, and varies somewhat with the kind of resin oil used.

If α_D be the rotation observed in a 100 mm. tube, and p the weight of resin oil contained in the mixture, the value of the latter is given by the formulæ—

$$30 : 14° :: p : \alpha_D.$$

$$p = \alpha_D \frac{30}{14}, \text{ for refined resin oil.}$$

$$p = \alpha_D \frac{30}{17}, \text{ for best white resin oil.}$$

$$p = \alpha_D \frac{30}{21}, \text{ for fine rectified resin oil.}$$

The first is the kind most commonly employed. A 100 mm. tube is used in preference to a 200 mm. one, on account of the dark colour of the oil. If it be required to examine paint for it, a quantity of the paint is shaken up with ether, and the rotation given by the ethereal solution observed in a 200 mm. tube. J. H.

SUGAR OF LEAD. *Lead acetate v.* ACETIC ACID.

SUINE. A butter substitute made from pigs' fat *v.* MARGARINE.

SULPHOCYANATES or **THIOCYANATES** *v.* CYANIDES. These salts are finding increased application for various purposes in dyeing and printing, as well as for the manufacture of colours. The sulphocyanates are not generally obtained from gas liquor, unless the latter has a sp.gr. corresponding to 10–15°Bé., and this being of rare occurrence, 'Laming's ferric oxide mass' has been used of late years for their preparation. As it sometimes contains 10 to 12 p.c. of ammonium sulphocyanate, this salt is always mixed with other ammonium salts, and the best method of separation—viz. that of partial crystallisation —is attended with considerable difficulty and loss. Numerous patents have been taken based on the preparation of sulphocyanides from the residue of Laming's mixture, with subsequent removal of the sulphur of the compound and formation of ferrocyanides. The manufacture of sulphocyanates can only be carried on profitably in works where other cyanogen products, such as ferrocyanides, Prussian blue, &c., are prepared (F. Nafzger, C. Z. 10 370 ; S. C. I. 324).

SULPHOLEIC ACID *v.* OLEIC ACID.

SULPHONAL consists of *diethylsulphodimethylmethane* $(CH_3)_2C(SO_2C_2H_5)_2$, and was first prepared by Baumann. It forms colourless, heavy, prismatic crystals, and is given to adults in doses of 2 grms. as a soporific (B. Tischer, Pharm. Zeit. 33, 235 ; S. C. I. 7. 457).

Some difficulty is experienced in preparing an odourless product. According to Kobbe, it is easy to determine whether a preparation is odourless or not by boiling 1 grm. with about 10 c.c. of water in a test tube, when any remaining odour is easily detected (Kobbe, Pharm. Zeit. 1888, 730 ; S. C. I. 8, 131).

Sulphonal may be identified as follows : It melts at 125·5°, dissolves in 15 parts of boiling water, and 500 parts of water at 15° ; in 133 parts of ether at 15°C. ; 2 parts of boiling alcohol, 65 parts of alcohol at 15° ; and in 110 parts of 50 p.c. alcohol at 15°. The sample should also be tested for sulphuric acid, potassium, and manganese. It is exceedingly inert towards all re-agents, a characteristic property of the substance. Fused with potassium cyanide, it gives a smell of mercaptan. Mercaptan, according to Ritsert, may be formed by heating sulphonal with sodium-amalgam or pyrogallic acid. Fused with dry potash, a peculiar smell of mustard oil is evolved. Mercaptan is also formed by heating the substance in a test tube with a fragment of charcoal ; the white fumes which are at the same time given off turn litmus-paper red, and decolourise blue iodide of starch paper (S. C. I. 1888, 772).

SULPHUR. This element usually occurs in commerce in two forms : one a crystalline powder, 'flowers of sulphur,' prepared by rapidly cooling the vapour formed during the distillation of crude sulphur or substances containing it, so that condensation to *solid* particles ensues, much as snow is formed by quickly chilling aqueous vapour ; the other as lumps and blocks of 'brimstone,' obtained by fusing sulphur, and allowing it to solidify in moulds, so as to form cylindrical or slightly conical 'sticks' or 'rolls,' or masses of larger magnitude. For a short time after solidification such cast masses consist of aggregations of more or less well-defined crystals belonging to the oblique prismatic system ; but these gradually change their character and become transformed into an assemblage of smaller crystals, consisting of octahedra with a rhombic base ; sulphur being *dimorphous*, or capable of crystallising in two entirely distinct forms, of which the octahedral form is the more stable at ordinary temperatures. Accordingly, when sulphur occurs crystallised in nature (as in certain volcanic districts), or when it separates from its solutions in *cold* solvents by their evaporation (*e.g.* from carbon disulphide solutions), it always assumes the rhombic octahedral shape. On the other hand, from *hot* oil of turpentine solution it crystallises in the prismatic form ; whilst artificial or natural octahedral crystals immersed in an inert liquid, the temperature of which is gradually raised to above 100°C., but below 115°C. (near the first melting-point of sulphur), become opaque, owing to their becoming changed into aggregations of small prismatic crystals ; indicating that at temperatures near to 100–115° the prismatic form of crystal is the more stable of the two. The two kinds of crystal differ in relative density, the octahedral form being 2·05 times as heavy as water, and the prismatic variety only 1·98 times as heavy ; the latter evolves more heat on combustion than the former, so that heat is evolved in the transformation of prismatic into octahedral crystals.

Owing to this change in crystalline structure taking place after solidification, cast sulphur (brimstone) is excessively brittle, being a bad conductor of heat ; if grasped in a warm hand it crackles, and often breaks up into fragments in consequence of the strain produced by unequal expansion. Both forms of crystal dissolve freely in carbon disulphide, and to a greater or lesser extent in various other solvents—notably, sulphur chloride, turpentine, benzene and other petroleum and coal-tar hydrocarbons, alcohol, chloroform, &c. Methods of extraction of sulphur from natural sources, where it is intermixed with much earthy and rocky matter, based on the employment of such solvents have been proposed, but not as yet very extensively adopted. When a powerful beam of sunlight, concentrated by a lens, is passed through a solution of sulphur in carbon disulphide contained in a closed vessel, partial conversion into an insoluble modification is brought about, so that a turbidity forms in the path of the light due to the separation of minute particles of *insoluble sulphur* ; the emergent light is destitute of the ultraviolet rays, whereas the less refrangible luminous part of the spectrum is unaltered ; apparently, therefore, the chemical rays are absorbed and expended in the production of intra-molecular work, the change presenting many points of similarity to the conversion of yellow phosphorus into red, when a solution of the former in carbon disulphide, ethyl iodide, or analogous solvents is exposed to light, whereby a separation of the other modification insoluble in these solvents is brought about.[1]

Octahedral sulphur crystals begin to melt at 114·5°, whilst prismatic sulphur melts and re-solidifies at 120° if perfectly pure ; but if containing traces of the plastic modification it begins to melt at 111·5° (Brodie). Natural rhombic crystals have been described by Silvestri, melting at 121–125°. At temperatures but little above 120° the limpid fluid obtained by fusing any solid modification of sulphur remains apparently unchanged ; on cooling cautiously out of contact with dust, it shows the phenomenon of superfusion very distinctly, and under these conditions will solidify to prismatic crystals if a crystal of prismatic sulphur be dropped in to serve as nucleus, and to octahedral crystals if a fragment of octahedral sulphur be similarly added. If heated somewhat above 120° conversion into a peculiar allotropic modification termed *plastic sulphur* commences ; at higher temperatures the action proceeds more rapidly, so that at 200–250° a thick viscid mass of dark brownish-red colour is obtained, which, if quickly cooled in water, forms a red plastic dough-like mass, insoluble in carbon disulphide, but gradually changing on standing into a crystalline mass, mainly consisting of octahedral soluble sulphur. If more quickly cooled by means of a mixture of ether and carbon dioxide snow it forms a hard transparent mass, becoming plastic at the ordinary temperature. At temperatures above 250–300° viscid sulphur becomes thinner, though not as fluid as melted brimstone at 120°; and at 440° it boils, giving off orange-coloured vapours. According to the earlier researches of Bineau, Dumas, and others, at temperatures near to 500° the vapour is 96 times as heavy as hydrogen, indicating that it is composed of hexatomic molecules S_6; but at 1,000° these break up into diatomic molecules S_2, so that the vapour is then only 32 times as heavy as hydrogen. More recent experiments by Biltz (B. 1888, 2,013) have, however, shown that no constant vapour densities are observed at any lower temperatures, and that molecules S_7, S_5, S_n, are just as clearly indicated as S_6; a continuous dissociation and lowering of vapour density taking place as the temperature rises until only S_2 molecules exist.

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[1] [illegible]

Besides the amorphous solid modification insoluble in carbon disulphide above mentioned, a soluble amorphous variety exists, obtained by the action of acids on solution of alkaline polysulphides. This is employed medicinally under the name of *milk of sulphur*; on keeping, it slowly changes into the octahedral crystalline variety. Flowers of sulphur condense from the vapour of sulphur, at first as *utricles*, or liquid droplets surrounded by solid pellicles; these gradually become octahedral crystalline sulphur, but generally a little of an insoluble modification is left behind on treatment of flowers of sulphur with carbon disulphide, and the same remark applies to plastic sulphur that has changed by standing into a brittle mass. The presence of small quantities of other bodies considerably modifies the colour and texture of amorphous sulphur and its properties; thus, black, red, and blue varieties are obtainable, as also a green liquid (for a time) at ordinary temperatures. All these varieties become converted into ordinary brimstone by fusion. When hydrosulphuric acid solution is electrolysed, sulphur appears at the positive pole in the form of a soluble amorphous variety; whilst an insoluble form is obtained when sulphurous acid solution is electrolysed, separating at the negative pole: accordingly Berthelot classes the soluble modifications (including the crystalline forms) and the insoluble ones as *electro-negative sulphur* and *electro-positive sulphur* respectively.[1] The latter forms possess more intrinsic chemical energy than the former, and hence evolve heat on passing into the crystalline state. They also have lower relative densities, varying from 1·82–1·87° (utricular amorphous sulphur) to 1·95 (ordinary plastic sulphur). Debus has recently described a colloidal form of sulphur analogous to the soluble silica obtained by dialysis; this is contained in Wackenroder's solution, formed by passing sulphuretted hydrogen through solution of sulphurous acid (C. J. Trans. 1888, 278).

The amorphous forms of sulphur meet with but little application in the arts; plastic sulphur is used to a limited extent as a material for preparing moulds for electrotyping and other purposes, and precipitated 'milk of sulphur' as a medicinal preparation. In the 'recovery' of sulphur from alkali waste by various processes amorphous sulphur is obtained as a precipitate; this, however, is not collected as such, but is melted by the aid of superheated steam or under high-boiling saline solutions, so as to form ordinary brimstone (*v. infra*). Flowers of sulphur are mainly employed for dressing vines, so as to preserve them against the *oïdium* disease, also for treating hops and seeds of various kinds, and for vulcanising indiarubber; and brimstone as a source of sulphur dioxide for bleaching and disinfecting purposes, for the production of bisulphites in the manufacture of wood pulp for paper-making, and in the manufacture of sulphuric acid; but moderate quantities of sulphur are consumed for many other purposes—*e.g.* the preparation of vermilion, sulphur chloride (for vulcanising), and carbon disulphide, the manufacture of gunpowder and matches, &c.

Sources of sulphur.—Sulphur is chiefly obtainable from three classes of natural products—namely,

(I.) *Free sulphur*, usually, though not invariably, found in volcanic districts. Deposits of this class are of two kinds (*a*) 'living' sulphur beds, *i.e.* localities where sulphur is being continously deposited by virtue of certain chemical actions perpetually going on; such a place is termed a 'solfatara,' and is ordinarily associated with eruptive craters, geysers, hot springs, 'fumaroles' (or jets of steam and sulphurous and other vapours issuing from crevices), and similar evidences of present or recent volcanic action; (*b*) stratified deposits (more or less alternating with beds of clay and other minerals), mostly consisting of sulphur to the extent of 5 to 40 p.c., the majority being calcareous or other earthy matters.

(II.) *Sulphur combined with metals as sulphides.* These minerals constitute many of the most important metallic ores, *e.g.* pyrites, copper pyrites, galena, zinc blende, cinnabar, stibnite, &c., respectively the sulphides of iron, iron and copper, lead, zinc, mercury, antimony, &c. Some of these substances evolve sulphur on heating, and in consequence were formerly used to some considerable extent as sources of free sulphur; but at the present day for the most part metallic sulphides are not employed directly in this way to produce sulphur, but rather to generate various sulphur compounds, more especially sulphur dioxide (by roasting in contact with air) used for the manufacture of vitriol.

(III.) *Compounds of sulphur with metals and oxygen forming sulphates.* Of these the sulphate of calcium is probably the most abundant, large deposits of this salt in the anhydrous form, and crystallised as gypsum, being found in numerous localities, whilst it is an almost invariable constituent of well, river, lake, and sea waters. Sulphates of magnesium, barium, and many other metals are also substances of common occurrence. Processes for the isolation of sulphur from these sources have been devised, but hitherto not employed to any considerable extent, the other sources of sulphur being practically cheaper. Besides these substances many other natural products, from living as well as mineral sources, contain more or less sulphur.

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[1] According to R. Weber both the soluble and insoluble amorphous forms are always produced together, either by electrolysis or chemical reactions, the one or the other predominating according to circumstances.

As regards the original sources of these substances some doubt exists as to whether metallic sulphides are to be regarded as being the prime source of the sulphates formed therefrom by oxidation; or whether, on the other hand, they have not been deposited from solutions containing sulphates and soluble metallic compounds under the reducing influence of organic matter; both kinds of reaction are known to take place naturally, the production of green, blue, and white vitriol (sulphate of iron, copper, and zinc respectively) by the spontaneous oxidation of pyrites, copper pyrites, and zinc blende, often together with alum and other sulphates, having been known for many centuries; whilst the formation of sulphurous waters (containing sulphuretted hydrogen and soluble sulphides), and the deposition therefrom of free sulphur and insoluble sulphides, by the inverse chemical changes, is also a very commonly occurring phenomenon. The free sulphur of volcanic districts has been produced to some extent by reactions of this latter class, more especially in the case of stratified deposits; a portion owes its origin to the combined effect of heat, moisture, and oxygen on beds of metallic sulphides, especially pyrites, whereby sulphur is partly directly volatilised and partly formed in virtue of more complex reactions (*e.g.* in the Kohat district of the Punjab, where a large amount of sulphur is continually being deposited as a result of the decomposition of pyritiferous alum shales); but the majority of the sulphur deposited in *solfataras* owes its origin to the mutual reaction of various gases and vapours formed underground and escaping into the air through clefts and crevices forming 'fumaroli.' The deposition of sulphur in this way is due to two different reactions; in some cases currents of gases containing on the one hand sulphur dioxide, and on the other sulphuretted hydrogen, intermix, producing mutual decomposition of the two gaseous sulphur compounds, thus: $SO_2 + 2H_2S = 2H_2O + 3S$. In other instances sulphuretted hydrogen comes in contact with air under such conditions that only the hydrogen is oxidised, sulphur being set free, thus: $H_2S + O = H_2O + S$. This latter action is greatly facilitated by contact of the gases with various kinds of solid matter, notably ferric oxide; and in this form is the most important portion of certain processes recently introduced for the recovery of sulphur from gas liquor, vat waste, and similar materials (*v. infra*). Not improbably this action really involves two stages—namely, first, where the sulphuretted hydrogen is partly oxidised to water and sulphur dioxide, thus: $H_2S + 3O = H_2O + SO_2$; and second, where the sulphur dioxide thus produced reacts whilst nascent on the rest of the sulphuretted hydrogen, forming water and sulphur as above described; for if more air be present than will furnish oxygen sufficient to convert the hydrogen of the sulphuretted hydrogen into water, sulphur dioxide is formed, as well as free sulphur; whilst if less be present, unchanged sulphuretted hydrogen escapes.

As to the nature of the chemical changes taking place underground, in virtue of which gaseous sulphur compounds are formed, but little definite knowledge is extant. Water percolating at great depths, and consequently under high pressure, into seams containing metallic sulphides, *e.g.* pyrites, is likely enough to form sulphuretted hydrogen and metallic oxides; the former may also be produced by the reduction of sulphates dissolved in water under the influence of heat, pressure, and organic matter. Sulphur dioxide, again, may result from the complete oxidation of sulphuretted hydrogen thus formed; by the action of heat and oxidising agents on metallic sulphides; or by the mutual reactions of sulphides and sulphates, as in the process of lead smelting, thus: $PbSO_4 + PbS = 2Pb + 2SO_2$. From the usual presence of steam in the fumes and vapours emitted from living solfataras, it would seem more probable that water vapour is generally involved in the chemical changes taking place, than that the action is one of the last kind taking place at a high temperature in the absence of water.

Some few stratified sulphur deposits have probably been formed by analogous actions taking place underground between gases and vapours passing through porous strata so as to deposit sulphur therein; but aqueous agencies have more frequently been at work. By the reducing action of organic matter on sulphates, sulphides are readily formed; when calcium sulphide is thus produced together with carbonic acid decomposition takes place, so that sulphuretted hydrogen and calcium carbonate or bicarbonate are formed:

$$CaS + 2H_2O + 2CO_2 = CaCO_3,H_2CO_3 + H_2S.$$

Water charged with sulphuretted hydrogen produced in this or some similar fashion when exposed to air deposits sulphur, the hydrogen of the sulphuretted hydrogen being oxidised to water: $H_2S + O = H_2O + S$. In presence of ferric oxide (as, for example, when the water contains ferrous bicarbonate, which becomes ferric hydroxide on exposure to air) this action goes on rapidly, the ferric oxide acting as a carrier (as in the processes of coal-gas purification by iron oxide revivified by exposure to air, and in Claus' method of preparing brimstone from sulphuretted hydrogen—*v. infra*); whilst if calcium bicarbonate be present in the water, exposure to air converts this into ordinary insoluble carbonate, so that a deposit of sulphur mixed with calcium carbonate results. The Sicilian sulphur deposits appear to have mostly been formed in this way in the beds of lakes into which such sulphurised and calcareo-carbonated waters ran: now and then changes in the character of the water caused other deposits (clay, marl, &c.) to form, so that layers of sulphur rock (mainly carbonate of lime and sulphur) alternate with layers of other minerals. Reactions somewhat similar to this are going on at the present day; thus a notable formation of sulphur takes place continually at the dried-up margins of the tidal swamps at the mouth of the Godaveri, Madras, gypsum being reduced to sulphide by the organic matter, and calcium carbonate and sulphur being then formed by the conjoint agency of the air and carbon dioxide; and similarly, free sulphur is copiously formed by the action of the air on alkali waste containing sulphide of calcium, this sulphur generally combining with unaltered calcium sulphide to form a soluble polysulphide. Under certain conditions calcium carbonate will react on sulphuretted hydrogen in presence of air, so as to form calcium sulphate and free sulphur (Bischof); possibly thus:

$$CaCO_3 + 2H_2S + 5O = CaSO_4 + CO_2 + 2H_2O + S.$$

Some sulphur deposits appear to have been produced in accordance with changes of this character, calcium sulphate and not carbonate chiefly accompanying the sulphur. By continued exposure to air calcium carbonate mixed with sulphur oxidises to calcium sulphate; the outcrops of seams of sulphur rock in Sicily are usually thus altered, the free sulphur having mostly all disappeared, and a material of peculiar character, known as *briscale*, been formed by the weathering action, the occurrence of which is looked upon as a certain sign of the existence of a lode of sulphur rock.

Certain natural metallic sulphides, especially pyrites, when subjected to heat, part with a portion of the sulphur present, so that by subjecting them to distillation sulphur may be obtained. Processes based upon this property have been somewhat extensively employed in the manufacture of brimstone; but the article thus produced is liable to be very impure, and, notably, to contain much arsenic. Accordingly, metallic sulphides are far more frequently employed to produce sulphur dioxide by combustion (for the manufacture of sulphites, saltcake, vitriol, &c.) than as a source of actual free sulphur. Of late years an indirect method of obtaining sulphur from such sources has come into use as an adjunct to the alkali manufacture by Leblanc's process. In this manufacture pyrites is first converted into sulphuric acid, which, reacting on salt, forms hydrochloric acid and sulphate of sodium (saltcake); or saltcake is formed more simply by passing sulphur dioxide and air through masses of salt loosely piled, the gases being formed by the combustion of pyrites in presence of excess of air. The saltcake is then fluxed together with small coal and carbonate of calcium, whereby carbonate of sodium is produced and sulphide of calcium; the former being soluble in water is thus dissolved out, whilst the latter remains insoluble and constitutes the main ingredient in 'vat waste.' Numerous processes have been invented for the economical extraction of the sulphur contained in this material, both for the sake of profit, and in order to get rid of a valueless and noxious by-product; but till recently these have practically met with only partial success. Recent improvements, however, have been effected whereby it becomes commercially practicable to isolate the sulphur in the form of brimstone, the essential reactions being the conversion of the substances into solid carbonate of calcium and gaseous sulphuretted hydrogen, by means of carbon dioxide produced in lime-kilns, and the partial combustion of this gas so as to form water and free sulphur, much as is naturally effected in certain natural fumaroles (*v. infra*; also SULPHURIC ACID).

Analogous processes are also available for the isolation of the sulphur contained in the evil-smelling 'gas liquors' produced in the manufacture of coal gas; the sulphur is contained in coal mainly as pyrites, probably produced by the reduction of sulphates in presence of ferruginous matter by the organic matter of the coal from water percolating through it; the quantity so extracted is but small as compared with that used in the form of pyrites for vitriol manufacture, but still a notable amount of sulphur is thence obtainable. Where the cost of the process is not prohibitive, sulphur might be readily obtained from natural sulphates, such as gypsum, by first reducing them to sulphides, and then applying the same methods of sulphur-extraction; but the plentiful supplies of natural sulphur and pyrites now obtainable render these materials far cheaper than sulphur prepared from gypsum can possibly be; so that various processes invented at different times for extracting sulphur from such sources are not in actual use.

I. NATURAL SULPHUR.

As already stated, free sulphur occurs naturally in stratified rocky deposits, from which it is obtained by the ordinary methods of mining and quarrying, supplemented by processes for separating the sulphur from the stony matter accompanying it; and in surface deposits which have been produced by the solfataric actions above described, and which in many cases are still 'living'—*i.e.* the sulphur-depositing agencies are still at work; so that successive crops, so to speak, of sulphur can be obtained from the same ground after appropriate intervals of time have been allowed to elapse. Both kinds of deposit are rarely, if ever, met with in quantity, except in regions where volcanic influences either are still at work, or have been so recently; but such districts are tolerably frequently met with. In Europe, Italy and Sicily have long been the chief sources of supply; a bed of sulphur rock occurs in France in the department of Vaucluse, and several deposits, some of which are worked, are found in Spain. In Turkey several sulphur mines exist; whilst in Austro-Hungary large sulphur deposits are found, the whole district around Mount Büdös in Transylvania being rich in sulphur formed by living solfataric action. In Iceland large solfatara fields exist, some of which are being exploited commercially. Near Suez sulphur rock (in one place 600 feet thick) is found, whilst an important deposit occurs near Tripoli; in China, Formosa, the Banda Islands, numerous places in India, Kashmir, and Burmah, in Japan, the Philippine Islands, and the Sunda Islands, more or less copious deposits are found; also in several of the United States, notably in California, Nevada, and the Yellowstone district of the Rocky Mountains; beds of nearly pure sulphur, upwards of 100 feet thick, have been recently found by boring in Louisiana; whilst living or extinct volcanic craters, in which considerable quantities of sulphur exist, occur in many parts of the world.

Various methods for the separation of natural sulphur from accompanying earthy and rocky impurities have been and are still employed; these may be classified as follows:—

A. *Liquation processes.* Where the sulphur is melted so as to run away and separate from the unfused earthy matter. These are of four kinds, viz. (1), processes when the heat is obtained by the combustion of part of the sulphur present; which method, though wasteful as regards sulphur, is so cheap as regards labour that it is still employed to a larger extent than any other; (2) processes where the heat is obtained by the use of other extraneous fuel (wood, coal, &c.)—these are only used for very rich materials, or for refining crude sulphur; (3) processes where the sulphur is melted out under a liquid of high boiling-point, *e.g.* concentrated chloride of calcium solution; (4) the steam process, where high pressure or superheated steam is the source of heat.

B. *Distillation processes.* Chiefly employed for refining crude sulphur, or for rich ores, where the sulphur is volatilised in a kind of retort, and the vapour condensed either as flowers or as melted brimstone.

C. *Solution processes,* where a solvent (carbon disulphide) is employed to dissolve out the sulphur. By employing a series of lixiviation vessels worked systematically, fresh solvent comes in contact with nearly exhausted ore, whilst fresh ore is treated with solvent already containing much sulphur, so that a nearly saturated solution is obtained, from which the solvent is recovered by distillation, much as in the processes for extraction of oil, grease, &c., from seed-cake, greasy rags, and such like materials (*v.* CARBON DISULPHIDE).

A. *Liquation processes.* Sulphur scraped from the surface deposits of fumaroles &c., or otherwise moderately free from admixed earthy impurities, is sometimes purified by the simple process of fusing it in a pot or cauldron, heated by a fire underneath (taking care to avoid firing), allowing impurities to subside, and ladling out the clarified sulphur into moulds. Such material, however, is usually suitable for direct distillation to form flowers and purified brimstone, and is more usually worked up in that way, so that the old 'pan' process of melting is now comparatively rarely employed, except in certain localities out of the way of European trade. According to Warnford Lock (Journal Soc. Arts, 1884, p. 792), the method involving a similar mechanical separation of impurities by fusion under a concentrated solution of calcium chloride boiling at about 115°C, is virtually a failure, as 'the very slight difference in specific gravity between the sulphur and the associated impurities from which it has been melted out practically precludes any real separation taking place.' C. Vincent, however, reports favourably on the process when the liquor used is of boiling-point not less than 120°C. (Bl. 40, 528). When superheated steam is substituted for the aqueous solution of calcium chloride much better results are attained; in Nevada and California, and to some extent in Italy and Sicily, this process has been successfully adopted, the apparatus used consisting essentially of a cylindrical or slightly conical iron vessel about ten to twelve feet high coated with non-conducting material, and divided into an upper and a lower compartment by a horizontal sheet iron diaphragm perforated with holes (fig. 1). A charge of about 2 tons of ore is introduced into the upper compartment, and steam of 60 to 70 lbs. pressure supplied, so that the temperature rises to 111°C. and upwards; the sulphur then melts, and runs down through the diaphragm into the lower compartment, whence it is drawn off from time to time. Ores too poor to be worked successfully in any other way can in many cases be profitably treated by the steam process, as the loss of sulphur through oxidation is *nil*, whilst only a small quantity remains in the exhausted ore; but the cost of working is far greater than in the older liquation processes,[1] where the heat generated by the combustion of part of the sulphur in a mass of piled-up sulphur rock is employed to melt out the rest of the sulphur; accordingly these processes are still those most extensively employed in Europe, notwithstand the two-fold disadvantage that much sulphur is necessarily lost as escaping sulphur dioxide formed by combustion, and that this sulphur dioxide acts most deleteriously on crops and vegetation; so that the combustion process in many cases cannot be worked continuously all the year round, but only in the winter months, after the harvest has been gathered in and before the spring fairly commences.

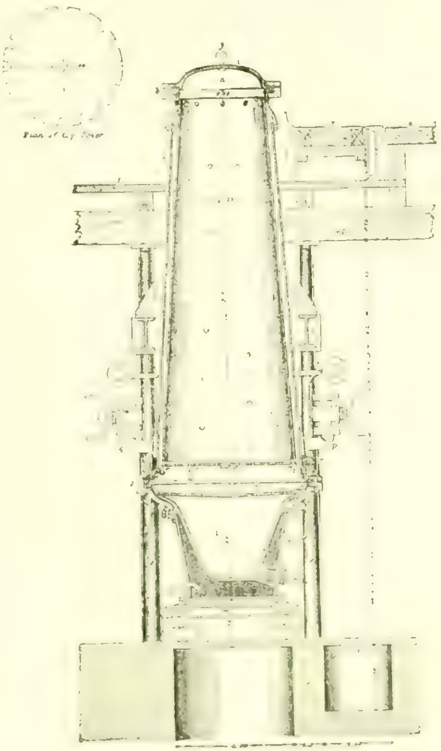

FIG. 1.

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[1] [illegible]

Formerly the heaps of sulphur rock thus treated were of comparatively small size—only a few feet in diameter (*calcarelle*); but these small stacks have now been generally superseded by much larger, partially walled-in kilns (*calcarone* or *calcherone*), which are less wasteful. In the calcarelle system, the ground on the side of a slope is beaten hard to render it impervious, and the stack built up with larger lumps at the base and somewhat smaller pieces in each successive layer, in such a fashion that the lowest point of the slope on which the stack stands forms an angle, the soil being banked up a few inches all round the base; or else the ground being somewhat trenched out, so as to form a kind of saucer, in which the stack is built. The heap being fired on the top and air having free access all round, combustion goes on rapidly, so that all the sulphur in the rock at the external portions of the heap is consumed, and only that from the central portion melted out without oxidation; this fused sulphur runs down the sloping floor to the lowest portion of the trench, where a rough doorway (*morto*) of lumps of stone not containing sulphur allows its egress to wet wooden ingot moulds, in which it is cast into cakes weighing about 50 kilograms (1 cwt.) (*balate*). Much the same arrangement, on a larger scale, is employed in the calcarone, saving that here a masonry retaining wall several feet high is built up round a sloping circular bricked sole (in some cases only round the lower half of the floor), whilst the stack is covered over with *genese* (spent smalls from previous operations), so as to exclude air, excepting that entering through orifices or rough chimneys built up in the stack for the purpose with larger fragments of sulphur rock. The heap is fired by means of bunches of grass, &c., dipped in sulphur, thrown down these openings, or at the back when not entirely surrounded by a wall, and the melted sulphur produced drawn off through the morto, either continuously or by tapping at intervals. A calcarelle containing some 4 to 6 tons of material, requires only about 3 days to build up and work off, the yield of sulphur being rarely more than one-fourth or one-fifth of that contained in the rock treated, when this contains 30–35 p.c. of sulphur; whilst a calcarone containing 200 to 2,000 tons requires from 1 to 3 months, and yields, under favourable conditions, not far from two-thirds of the sulphur originally present in the form of balate or ingots. The time of working and yield are naturally much influenced by the weather and nature of the rock. Heavy rains interfere seriously with the working by lowering the temperature, whilst a sirocco is apt to cause an unduly rapid combustion of sulphur on the side where the wind impinges. Again, some varieties of sulphur rock burn and liquate much more readily than others. When air has access to calcareous sulphur seams, as near their outcrop, oxidation and formation of calcium sulphate occurs, forming gypsum as a disintegrated mass, termed *briscale*. When gypsum is contained in the material liquated loss of sulphur occurs from two causes, especially towards the end, when the temperature is highest: firstly, heat is caused by vapourising the water of crystallisation—*i.e.* more sulphur must be burnt to supply the requisite heat; and, secondly, sulphur and calcium sulphate react on one another, forming calcium sulphide and sulphur dioxide, thus—

$$CaSO_4 + 2S = CaS + 2SO_2.$$

Calcium carbonate and sulphur similarly form calcium sulphide and sulphur dioxide at high temperatures. An improved form of calcarone has been introduced by P. Le Neve Foster, where the heat generated in a heap built up in the ordinary way is utilised to liquate a second mass of rock in a brickwork kiln at its back. The products of combustion in the heap at first pass off, and the sulphur is collected in the ordinary way; but when the process is finished the heat of the residual ignited mass is employed to raise the temperature of a current of air drawn into the kiln by a flue communicating with the base of the heap. The oxygen of this air mostly becomes sulphur dioxide by burning off the small amount of residual sulphur in the heap, so that the kiln is fed with a stream of hot gases, which liquate the sulphur from the rock in the kiln without wasting it to any great extent by oxidation (Warnford Lock, *l.c.*). Durand's kiln is an ordinary calcarelle, some 6 or 7 feet square, surrounded by a masonry wall, with door-holes for discharging spent material, and covered in with an arched roof, with a charging-hole in the centre. The liquated sulphur runs off in the usual way, whilst a small additional quantity is condensed in a flue through which the products of combustion are made to pass. Obviously, a covered-in kiln permits of easy regulation of the air supply, and its action is independent of the weather, but the cost of construction and working is greater than in the case of open stacks. K. Walter has patented a form of apparatus whereby the sulphur dioxide formed during the combustion of part of the sulphur is utilised for the manufacture of sulphuric acid (Z. 1886, p. 1199).

B. *Distillation processes.* In certain Eastern localities the native sulphur is separated from intermixed calcareous matter, &c., by a process of distillation, or sublimation, in earthen pots, one heated by a fire serving as alembic, and another, inverted over it, as condenser. In Europe smalls too fine to burn in calcarone are sometimes distilled in a series of iron vessels (*doppione*), arranged in a double row, heated by a gallery furnace (fig. 2), the vapours being received in condensers after passing through long slanting iron connecting tubes, one condenser sufficing for two distilling vessels; but this apparatus is more frequently employed to purify the crude sulphur run out from the calcarone. When flowers are manufactured the appliances used consist of a pair, or larger set, of retorts, something like those used for coal gas, in which

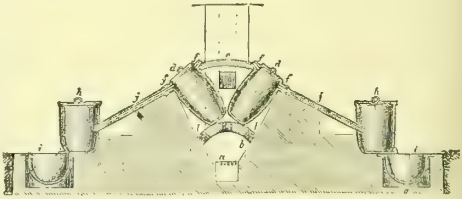

FIG. 2.

the brimstone is vapourised, the vapour passing into a capacious chamber, in which it condenses as flowers as long as the temperature is below the melting-point of sulphur. To supply each retort a pan at a higher elevation is arranged, heated by the waste heat, so as to keep brimstone just fused therein; this melted brimstone is allowed to flow into the retort by means of a valve closed by a plug, with a rod attached as a handle, whereby a continuous or intermittent supply can be obtained. If the process is worked for some time, the walls of the condensing chamber become so hot that the sulphur condenses in the liquid state, when either the distillation is stopped or else the liquid distilled sulphur is run off into conical moulds, and cast into 'rolls' or 'sticks.' In some localities (*e.g.* at Radoboi, in Croatia) the native sulphur rock is heated in retorts, and the evolved vapour led directly into a large condensing chamber, so as to produce flowers at the first operation; whilst at Swoszowice, near Cracow, tubular slanting retorts have been employed in such fashion that part of the sulphur was liquated, and ran away at the lower end, whilst the rest was volatilised and condensed. From ores containing about 10 p.c. of sulphur a yield of about 6$\frac{1}{2}$ p.c. was obtained.[1]

C. *Solution processes.* Bollman has proposed the use of carbon disulphide as a solvent for sulphur for the purpose of separating it from earthy matters, the extraction process being worked methodically, and the carbon disulphide being recovered by distillation, first at a gentle heat and then by superheated steam, so as to fuse the residue of sulphur left in the distilling vessel. The process was tried experimentally near Naples as far back as 1868, but hitherto does not appear to have been very extensively adopted. Warnford Lock (*l.c.*) gives a plan of a set of apparatus designed to treat 20 tons daily of raw sulphur material containing 50 p.c. of sulphur. Pelouze has proposed to use coal-tar oils as solvents instead of carbon disulphide, as being cheaper and less liable to loss through volatility. For laboratory purposes, especially the valuation of native sulphur rock, the disulphide process is a very convenient one, the amount of sulphur present in the sample operated on being either directly found by evaporation of the solvent, or inferred from the specific gravity of the solution (*v.* SULPHURIC ACID, p. 716). In the process of vulcanising various classes of goods, sulphur chloride containing more or less free sulphur in solution is employed; but such fluids are generally prepared from purified sulphur, rather than from the crude native material.

II. SULPHUR FROM NATIVE METALLIC SULPHIDES.

Several methods have at different times been used, to a greater or lesser extent, for the purpose of obtaining sulphur from sources of this kind. Of these the principal are:

(*a*) *The direct process of heating*, whereby sulphur is volatilised and obtained in the free state by condensation.

(*b*) *The combustion and reduction process*, where sulphides are roasted and the sulphur dioxide obtained again reduced by means of incandescent carbon, &c.

(*c*) *Conversion into volatile sulphur compounds, especially sulphuretted hydrogen, by heating in contact with organic matter*, and treatment of the gas produced, or of compounds thereof condensed by cooling the vapour evolved, in various ways, so as to obtain the sulphur therefrom.

(*d*) *Conversion successively into sulphur dioxide, sulphuric acid, saltcake, blackash, and vat waste*, and treatment of the latter in a variety of ways so as to extract the sulphur.

Processes of the first and second kinds are now but little employed, excepting as an adjunct to the manufacture of fuming sulphuric acid (*q. v.*), on account of the impurity of the sulphur obtained, considerable quantities of arsenic, amongst other things, being usually present. Processes of the third class are used to a considerable extent as regards the by-products formed in coal-gas making, in which industry the sulphur of the pyrites disseminated through the coal is largely expelled as sulphuretted hydrogen and other volatile compounds, and is partly collected as sulphide of ammonium, &c., in the ammoniacal liquors, partly removed from the crude gas by means of 'purifiers' of various kinds. Methods of the fourth kind have long been employed, not so much on account of the profit derivable from the extraction of the sulphur, as for the diminution of the nuisance caused in various ways by the accumulation of large quantities of vat waste in the vicinity of the works producing it; recent improvements, however, have enabled the extraction to be carried out highly profitably, or, what practically amounts to much the same thing, have caused a large reduction in the price of sulphur minerals, in view of the effect on the trade which would be produced by the extensive adoption of methods for the economical extraction of sulphur from vat waste.

(*a*) *Direct heating.* When pyrites FeS_2 is heated in the absence of air, somewhat less than one half of the sulphur contained is expelled, in accordance with one or other of the reactions

$$3FeS_2 = Fe_3S_4 + 2S.$$

$$7FeS_2 = Fe_7S_8 + 6S.$$

Formerly considerable quantities of sulphur were prepared, especially in Bohemia and Silesia, by heating pyrites in clay retorts arranged in a gallery furnace, the residual iron sulphide being oxidised by weathering, so as to convert it into sulphate of iron, utilised for the preparation of fuming sulphuric acid (*q. v.*). On roasting copper pyrites in heaps (somewhat after the fashion of the Sicilian calcaroni) a portion of the sulphur present is volatilised and condenses in the cooler parts of the mass, sometimes accumulating in cavities scooped out to receive it in the upper part, sometimes condensing in underground flues, when the heap is built on a brickwork floor with openings into the flues, and when well lit covered with sods, earth, &c., so that the products of combustion are made to traverse the flues. Various forms and dispositions of the heap, and various arrangements of floor, retaining walls, flues, and condensing chambers, &c., have been adopted, with different kinds of ore and in different countries; but for the most part these are but little used at the present day, the sulphur contained in such metallic ores being now more frequently converted into vitriol by roasting in appropriate kilns and conveying the gases to the vitriol chamber.

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[1] In [illegible] locally for making carbon disulphide, employed in the vine- [illegible] Arts Journal, 1885, 38).

(*b*) *Oxidation and reduction processes.* A number of processes have been proposed, all essentially based on the treatment of sulphur dioxide (prepared by roasting metallic sulphides or by burning sulphuretted hydrogen, &c.) with reducing agents at a moderately high temperature. Thus in 1839 Dyar and Chisholm took out a patent for the use of the mixture of hydrogen and carbon dioxide formed by the action of steam on hot coke, this being made to act on the gases from burning pyrites, the reduced sulphur being collected in a suitable condensing chamber. In 1843 Newton patented arrangements for the similar action of red-hot coke or gaseous hydrocarbons on pyrites gases; and in 1844 Lee patented the use of red-hot fuel for the similar reduction of the gases produced by burning sulphuretted hydrogen disengaged from vat waste, the gases being passed through a fire of ordinary coal or coke so arranged as to maintain at a red heat a flue or chimney filled with bricks, the products of combustion passing into this flue through interstices in the brickwork. The contact action of the brick surfaces (probably especially of ferric oxide therein) caused the interreaction of any undecomposed sulphur dioxide, and the sulphuretted hydrogen and carbon disulphide produced in contact with the fuel, so that little but free sulphur vapour resulted. In 1854 Spence patented a pyrites kiln containing a central vertical earthenware tube filled with coke, and so arranged that the products of combustion in the kiln passed downwards again through this tube, whereby the sulphur dioxide became largely deoxidised to sulphur; and shortly after he found that the same result could be brought about by simply mixing coke and pyrites in an ordinary kiln in alternate layers. None of these processes, nor various other analogous ones proposed by other inventors, appear to be at work to any notable extent at the present day,[1] excepting in so far as sulphur dioxide, produced by roasting pyrites, &c., is employed to react on sulphuretted hydrogen or alkaline sulphides (as in certain processes for extracting sulphur from alkali waste—*e.g.* Mactear's, *v.* p. 692), whereby the sulphur of the sulphur dioxide is ultimately obtained along with that derived from the other substances.

(*c*) *Sulphur from coal gas by-products.* These substances are essentially of two kinds, viz., the liquids obtained by the condensation of the vapours evolved during the carbonisation of coal, or the further scrubbing of the permanent gases so as to remove sulphur compounds therefrom; and the solid residues discharged from the purifiers. In the former the sulphur chiefly exists in the form of ammonium sulphide or sulphydrate, smaller amounts being present as sulphocyanide, &c.; in the latter the condition of the sulphur varies with the nature of the purifying agent. When lime is used the ultimate effect is to form calcium sulphydrate by the absorption of sulphuretted hydrogen, thus

$$\mathrm{CaO,H_2O + 2H_2S = CaS,H_2S + 2H_2O},$$

provided that carbon dioxide is absent; otherwise decomposition ensues, thus $\mathrm{CaS,H_2S + H_2O + CO_2 = CaCO_3 + 2H_2S}$. The calcium sulphydrate also absorbs carbon disulphide vapour, forming probably calcium sulphocarbonate $\mathrm{CaS,CS_2}$ or $\mathrm{CaCS_3}$, again provided that carbon dioxide is absent; otherwise this compound is decomposed thus $\mathrm{CaCS_3 + H_2O + CO_2 = CaCO_3 + H_2S + CS_2}$. Hence of a series of lime purifiers, the earliest will mainly contain calcium carbonate after long action, any sulphydrate and sulphocarbonate formed at first having been subsequently decomposed again by the entering carbonic acid; whilst the later ones will contain sulphydrate and sulphocarbonate, with little or no carbonate, the carbon dioxide having been all absorbed in the earlier vessels. When hydrated ferric oxide is used the action is quite different, ferrous sulphide and free sulphur being formed, thus: $\mathrm{Fe_2O_3,3H_2O + 3H_2S = 2FeS + S + 6H_2O}$. By exposing the sulphurised mass to moisture and air, the iron becomes again converted into hydrated oxide, with separation of sulphur, thus $\mathrm{2FeS + 3H_2O + 3O = Fe_2O_3,3H_2O + 2S}$, so as to be capable of use over again, this process of 'revivification' being carried out several times until the mass contains more than half its weight of free sulphur. From the product sulphur can be readily obtained as flowers or as brimstone by simple distillation; or the mass can be burnt in a specially arranged kiln for vitriol making, or otherwise utilised as impure sulphur. In actual practice it is usually found convenient to alternate lime purifiers with iron oxide ones, in such a fashion that the former remove all carbon dioxide from the gas before it enters the iron purifiers, where the sulphuretted hydrogen is mainly removed. Working in this way, carbon disulphide vapour is but little absorbed, so that supplementary purifiers are requisite containing lime that has largely been transformed into sulphydrate by the action of the crude gas, not continued so long as to cause the further decomposition brought about by excess of carbon dioxide; finally, the gas passes through an iron purifier to remove any traces of sulphuretted hydrogen liberated during the absorption of carbon disulphide.

Gas lime, consisting chiefly of calcium sulphide or sulphydrate, can be treated by sulphur recovery processes in the same way as vat waste (*v.* p. 690). Thus in 1861 A. Noble patented a method, involving much the same principles as Mond's and Schaffner's processes for treating the latter, consisting in submitting the liquor obtained by the action of water on vat waste or gas lime to the action of sulphurous acid, whereby sulphur is precipitated whilst calcium thiosulphate remains in solution. More frequently, however, gas lime is used as an insecticide manure, when practicable to dispose of it thus, it being in most localities a waste product apt to entail nuisance, and requisite therefore to be got rid of in the simplest way possible. Owing to the presence of sulphocyanides &c. in it, it is sometimes possible to utilise it in the manufacture of certain chemicals, but only rarely.

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[1] F. Bellingrodt describes (S. C. I. 1886, p. 534) a process for preparing sulphur by deoxidising sulphur dioxide by means of red-hot coke, used at Oberhausen in the treatment of a zinc blende containing mercury.

Ammoniacal gas liquor is of more importance as a source of ammonia than on account of the sulphur it contains; by scrubbing the crude gas over again with the ammoniacal liquor condensed in the earlier stage, a further quantity of sulphuretted hydrogen is removed, together with carbon dioxide, and a liquid obtained containing little, if any, free ammonia, but, instead, carbonate or acid carbonate, and sulphide or hydrosulphide, in such quantity that on heating to a temperature somewhat short of 100°C. these compounds are decomposed, and a mixture of sulphuretted hydrogen and carbon dioxide expelled, whilst the residual ammoniacal liquor is capable of being used over again after cooling to purify more crude gas, and so on continuously. A similar mixture of gases results when ammonium sulphate is made from gas liquor; for this purpose the liquors are boiled either alone or with lime, and the vapours evolved blown into 'saturators,' or lead-lined vessels containing sulphuric acid, so that ammonium sulphate is formed, whilst carbon dioxide and sulphuretted hydrogen are set free from the decomposition of the volatile ammonium salts passing over with the steam. Many attempts to utilise the impure sulphuretted hydrogen thus formed have been made; frequently avoidance of nuisance was the chief thing aimed at rather than profit, so that in such cases the issuing gases were simply passed through a fire so as to burn the sulphuretted hydrogen, the products of combustion being allowed to escape; in others, iron oxide purifiers were employed, which, however, required to be of enormous size on account of the large quantity of sulphuretted hydrogen and the comparatively slow action of iron oxide thereon. Farmer, in 1864, patented the use of the sulphuretted hydrogen thus obtained for vitriol-making, burning the gases to sulphur dioxide,[1] and passing this into the vitriol chamber; but the large quantity of carbon dioxide present rendered this practically a failure. Wallace and Claus, in 1877, proposed to treat sodium or potassium sulphide with the mixed gases so as to produce sodium or potassium carbonate, and almost pure sulphuretted hydrogen easily capable of use for vitriol-making; the carbon dioxide reacting on the alkaline sulphide precisely as above described on calcium sulphide. This process does not seem to have come into manufacturing operation; obviously it might be applied to gas lime (or vat waste when obtainable) as well as to alkaline sulphides. The most successful plan of dealing with such gases is that patented by Claus in 1882, in which a regulated stream of the gases containing sulphuretted hydrogen is mixed with a quantity of air containing just enough oxygen to combine with the hydrogen of that gas, the mixture being then passed through a peculiar 'kiln' or brickwork chamber containing hot ferric oxide; this acts as a carrier of oxygen from the air, so that ultimately (with a properly adjusted air supply) the hydrogen of the sulphuretted hydrogen is oxidised to water and the sulphur set free, the reactions being (so far as the oxide of iron is concerned) as follows:

$$xFe_2O_3 + H_2S = Fe_{2x}O_{3x-1} + H_2O + S$$
$$Fe_{2x}O_{3x-1} + O = xFe_2O_3.$$

At a temperature of about 200° this action goes on regularly, the heat liberated by the oxidation going on sufficing to maintain the temperature without the use of any other fuel. Previously many unsuccessful attempts had been made to obtain sulphur from the partial combustion of impure sulphuretted hydrogen (in some cases from gas by-products, in others from vat waste) by Blair,[1] Kopp, and others, the principal practical difficulty encountered being the irregularity in the composition of the mixture of gases dealt with, which prevented the proper regulation of the air supply, and thus led to loss of sulphur, either from excess of sulphuretted hydrogen being present which escaped unchanged, or from excess of air being supplied, whereby sulphur dioxide in excess was formed, which again escaped; in either case nuisance being created. This result also happens with Claus's kiln; but when suitable precautions are taken as regards the supply of sulphuretted hydrogen (more especially when a tolerably equable stream of gases is produced by running a continuous stream of gas liquor saturated with carbonic acid and sulphuretted hydrogen through a heating arrangement) there is said to be no practical difficulty in so exactly regulating the air supply that only inconsiderable quantities of gases containing sulphur escape, whilst the liberated sulphur is readily condensed as liquid brimstone, or even as flowers, though the amount of steam present in the vapours issuing from the kiln renders the former the more convenient course. Recently this process has been employed successfully by A. M. Chance in obtaining sulphur from sulphuretted hydrogen prepared from vat waste (v. p. 694). Either on account of the sulphuretted hydrogen thus obtained being more dilute, or for some other reason, it is very difficult to obtain the entire quantity of sulphur contained in the sulphuretted hydrogen in the free state; excess of air necessarily causes formation of sulphur dioxide, but even when this occurs, the reaction of this gas on sulphuretted hydrogen is not easily rendered complete, so that both sulphur dioxide and sulphuretted hydrogen are apt to co-exist side by side in the issuing gases, thus necessitating scrubbers or other auxiliary appliances to push the reaction further.

C. W. Heaton (Pat. No. 21,217, 1890) employs for this purpose a 'supplementary Claus kiln,' packed with oxide of iron or manganese; a sufficient volume of air is intermixed with the gases escaping from the ordinary kilns, and the whole passed through the supplementary kiln so as to convert all sulphur vapour, sulphuretted hydrogen, or other sulphur compounds present into sulphur dioxide, which is absorbed by an alkaline solution in a suitable scrubber with the production of a sulphite.

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[1] To insure proper combustion the [illegible] through an ordinary pyrite kiln or [illegible] phuretted hydrogen obtained as a [illegible] metallic sulphides (e.g. the [illegible] and on galena in the production of [illegible] has been successfully treated [illegible] Patent No. 1,298, 1880.

[1] Patent No. 313, 1858.

Analysis of spent gases from the Claus kiln. The gases escaping from a Claus kiln, used for preparing brimstone from sulphuretted hydrogen prepared by Chance's process, contain simultaneously sulphuretted hydrogen and sulphur dioxide, so greatly diluted by foreign gases (mainly nitrogen) that their mutual reaction takes place only extremely slowly. Crowther's method of analysis consists in passing the gas through solution of hydrogen peroxide, whilst another portion is simultaneously passed through iodine solution; the latter converts sulphur dioxide into sulphuric acid, with formation of hydriodic acid, and acts on the sulphuretted hydrogen, evolving sulphur, thus:

$$SO_2 + 2H_2O + I_2 = 2HI + H_2SO_4$$
$$H_2S + I_2 = 2HI + S,$$

whilst the former acts in accordance with the equations

$$SO_2 + H_2O_2 = H_2SO_4$$
$$H_2S + H_2O_2 = 2H_2O + S,$$

so that the sulphur dioxide is measurable by titrating the acidity of the fluid after the action due to the sulphuric acid formed; and by subtracting this from the iodine consumption the sulphuretted hydrogen is found. According to G. Lunge (S. C. I. 1890, 1018), the current of escaping gas carries away iodine from the fluid, so that the sulphuretted hydrogen is apt to be over-estimated unless the iodine is intercepted by a caustic soda absorption tube, the contents of which are added to the rest of the fluid before titration. But a preferable modification is to leave out the hydrogen peroxide treatment, and simply pass the gas through iodine with the additional soda tube containing standardised soda solution. The total fluid, if alkaline, is acidified with a known quantity of standard acid, and the iodine titrated with thiosulphate; after which the acidity is determined, using methyl orange as indicator, using decinormal solutions; if m c.c. be the iodine consumption (difference between iodine originally employed and thiosulphate originally used), and n (which must $< m$) the soda solution employed to absorb iodine, and o that used at the end to establish neutrality, then the sulphur present in the forms of sulphur dioxide and sulphuretted hydrogen are

$$\text{S in } H_2S \text{ and } SO_2 \text{ jointly} = \cdot 0016\, m$$
$$\text{S in } SO_2 \text{ alone} = \cdot 0016\, (n+o-m).$$

(*d*) *Extraction of sulphur from vat waste.* For many years attempts have been made to utilise the waste oxysulphide of calcium left undissolved when blackash is lixiviated, mostly based on its conversion into sulphur or sulphur compounds, either directly saleable themselves or capable of use in manufacture. Of these earlier attempts, those of Gossage are the most important, based on the production of sulphuretted hydrogen and its subsequent conversion into sulphuric acid. These experiments led to a series of patents being taken out in 1837 and subsequent years, the vat waste being decomposed by waste hydrochloric acid (at that time far less valuable than now) or by the acid manganese chloride solution from the bleaching powder stills, or by furnace or limekiln gases containing carbon dioxide, so as to form calcium chloride or carbonate and sulphuretted hydrogen, a series of decomposing vessels being employed in the latter case so as to insure the utilisation of practically all the carbon dioxide. The production of vitriol from the diluted sulphuretted hydrogen thus obtained proved in practice a failure, on account of the large bulk of nitrogen which rendered the gases produced by combustion too dilute for successful employment in the vitriol chamber, apart from various other inconveniences due to irregularity in the composition of the furnace gases &c. employed, and other causes. Attempts to concentrate the sulphur dioxide produced on burning by absorption in water, and then heating the liquid to expel the dissolved gas and obtain it free from nitrogen, also proved commercially unsuccessful; as also did processes for obtaining free sulphur from the sulphuretted hydrogen by making the gases react on ferric chloride solution, the reaction ensuing being $Fe_2Cl_6 + H_2S = FeCl_2 + 2HCl + S$, the acid ferrous chloride solution being then peroxidised by the action of air and used over again. No better success, commercially speaking, attended later attempts (1859) to produce sulphur by the mutual reaction, at a temperature of 120°F. (49°C.), of part of the sulphuretted hydrogen and the sulphurous acid produced by the combustion of the remainder thereof, or by the reaction of oxides of nitrogen upon sulphuretted hydrogen. Nor were various other inventors more successful than Gossage in utilising sulphuretted hydrogen from vat waste; *e.g.* Lee (1844), who burnt the gases and passed the products of combustion through red-hot coke so as to obtain free sulphur; Blair (1858), who burnt the gases in a limited supply of air so as to oxidise the hydrogen only of the sulphuretted hydrogen, and set free the sulphur; and Spencer (1859), who attempted to use the coal-gas iron oxide purifier system for vat waste gases. Recently, however, all the practical difficulties encountered by Gossage have been successfully overcome by Chance, by modifying the appliances used in such a way as to obtain a nearly equable supply of gas much richer in sulphuretted hydrogen than any obtained by Gossage, and of practically constant composition, so that its employment for vitriol-making can be profitably carried out (*v.* p. 694).

A mode of partially utilising vat waste was devised by Losh in 1852, based upon the spontaneous absorption of oxygen by the moist product when exposed to the air, whereby at a certain stage calcium thiosulphate is produced along with other substances. By lixiviating with water the oxidised waste and adding sodium carbonate (or sulphate) calcium carbonate (or sulphate) is precipitated, and sodium thiosulphate obtained by evaporation and recrystallisation of the crude crystals deposited. Only a small fraction of the sulphur contained in the vat waste, however, is thus obtained in the form of sodium thiosulphate; whilst, as the demand for that salt is limited, the process does not admit of widely extended use, although quite successful commercially as far as it has been adopted.

An entirely different process was patented by I. L. Bell shortly afterwards, consisting in smelting in a blast-furnace a mixture of burnt pyrites, vat waste, coke, and a little clay or flux, with the result of producing 'factitious pyrites,' or fused sulphide of iron, tapped out of the furnace at intervals. The difficulty experienced in burning this material, and various other causes, however, rendered the process commercially unsuccessful at the then price of pyrites, and it was given up after working to the extent of some 4,000 to 5,000 tons of factitious pyrites at a cost equivalent to about sixpence per unit of sulphur per ton (Transactions of the Newcastle-upon-Tyne Chemical Society, i., p. 117).

According to Kraushaar (D. P. J. 226, 412), when vat waste is subjected to the action of hot water at 5 atmospheres pressure, it breaks up largely into calcium hydroxide and sulphydrate, thus:

$$2CaS + 2H_2O = CaS,H_2S + CaO,H_2O.$$

The sulphydrate solution thus formed is useful in the leather industry; or it may be mixed with the liquid resulting from the atmospheric oxidation of vat waste so as to produce free sulphur on acidification, as in Mond's process (*vide infra*).

The tendency of vat waste to oxidise spontaneously in the air, forming successively polysulphides of calcium, thiosulphate and other less oxidised sulphur salts, and finally calcium sulphite and sulphate, has been long known, and many years before Losh employed this action as a commercial source of thiosulphates attempts had been made to utilise it for the isolation of free sulphur. Some of the earliest notable experiments in this direction were those of T. H. Leighton (1836), whilst many later ones were made by others, more especially by Townsend and Walker (1860), and Jullion (1861). But little success attended these attempts; between 1861 and 1865, however, the subject was taken up, on the one hand by Mond (working firstly under the direction of Guckelberger and subsequently on his own account), and on the other by Schaffner, with the result of the elaboration of two moderately successful processes exhibiting considerable similarity in general principles, but differing in details and the appliances employed to carry them into practice. In each case the leading feature is atmospheric oxidation up to a certain point, lixiviation with water to dissolve out soluble compounds, and treatment of the insoluble matter in the same fashion a second time, or more often successively; this alternate oxidation and solution being adopted instead of one oxidation only for a longer period, as in that case a much smaller yield of sulphur would be obtained through the larger formation of calcium sulphate. In this way liquors are obtained of more or less different composition, according to circumstances, polysulphides and hydrosulphides predominating in the earlier stages of oxidation, and thiosulphates being formed to a large extent latterly. By continual analysis of the products the progress of the oxidation can be checked at the right stage, and the constitution of each batch of liquors worked off can be determined, so that polysulphides, sulphydrates, and thiosulphates of calcium and sodium are contained in any given mixed lot of liquors in the right proportions, viz. when the bases (calcium and sodium) present as thiosulphates are as nearly as possible equivalent to those present in the form of polysulphides and sulphydrates. When this is the case, addition of an acid (hydrochloric acid usually) to the liquor causes the precipitation of sulphur in three ways, viz. (1) the decomposition of the thiosulphate, thus:

$$CaS_2O_3 + 2HCl = CaCl_2 + H_2O + SO_2 + S;$$

(2) the decomposition of the polysulphides, thus:

$$CaS_x + 2HCl = CaCl_2 + H_2S + (x-1)S,$$

and (3) the reaction of sulphurous acid formed in the first way (and by the decomposition of sulphite when present) upon the sulphuretted hydrogen evolved from the polysulphides by the second reaction, and from the sulphydrates when present, by the reaction

$$CaS,H_2S + 2HCl = CaCl_2 + 2H_2S;$$

the liquors consequently should be of such composition that on acidulation neither sulphuretted hydrogen nor sulphurous acid should be formed in excess.

Mond's process. In this process the alkali waste is treated in the tanks in which it is left after drawing off the soda liquors with a strong air-current introduced by a blowing engine under the false bottom of the tanks; rapid oxidation sets in, and the mass heats strongly. After some 14 or 16 hours the action has gone on to the most advantageous extent; the blowing is then discontinued and the mass lixiviated, first with weak liquor from a previous operation, thus forming strong liquor drawn off for use, and then with water, thereby producing weak liquors employed subsequently to lixiviate another batch. The blowing is then again proceeded with, after which the mass is again lixiviated and the process repeated, sometimes even a fourth or fifth time. Duplicate or triplicate sets of tanks are used, so that the lixiviation of blackash for soda may go on in one set whilst the others are in use for oxidation of the waste, each set being carefully cleaned out before being used again for soda lixiviation. Inasmuch as carelessness in cleaning leads to much damage of the soda liquors by formation of sodium sulphide, it is sometimes preferred to remove the waste from the soda lixiviation tanks to others in which it is separately blown, notwithstanding the greater cost for labour thereby entailed. If the blowing operations have been properly adjusted the resulting mixed strong liquors contain about twice as much calcium and sodium as polysulphides as they do in the form of thiosulphates, so that on the addition of hydrochloric acid the following is the chief change taking place (practically the sum of the three changes above-mentioned):

$$\begin{aligned} &2CaS_x + CaS_2O_3 + 6HCl \\ &= 3CaCl_2 + 3H_2O + (2+2x)S. \end{aligned}$$

If excess of sulphide is present, sulphuretted hydrogen is disengaged, and if excess of thiosulphate, sulphur dioxide; as the latter is less objectionable than the former, the liquors should be so regulated that if anything be in excess it should be the thiosulphate rather than the polysulphide. The decomposition is effected in an ordinary tank or tub at a temperature of 60-65°, so as to diminish the tendency to form calcium trithionate, and consequently calcium sulphate, which is apt to occur at the boiling-point in accordance with the reaction

$$5CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 2CaS_3O_6 + 4S$$
$$CaS_3O_6 = CaSO_4 + SO_2 + S.$$

To insure the proper composition of the liquors these are carefully analysed, and the blowing operations controlled by the aid of systematic tests of the resulting oxidised product. The deposited sulphur is collected on strainers and then melted by high-pressure steam in an autoclave, along with a little lime (to neutralise acid and dissolve arsenic), so as to form brimstone, which settles to the bottom and is blown off into a receiving vessel, whence it runs into moulds; this part of the treatment being essentially due to Schaffner, who devised a somewhat more complex piece of apparatus for the fusion.

Schaffner's process. The oxidation is here effected by exposure to air in heaps for some weeks; the mass is then broken up, and, after 24 hours' further exposure, is lixiviated. The insoluble portion is then again oxidised by exposure to air, or Mond's system of oxidation by an artificial blast blown through the mass after drawing off the liquors is adopted, and the oxidised mass again lixiviated, and the process repeated. Instead of treating the resulting liquors with hydrochloric acid in sufficient quantity to decompose all calcium salts at once, Schaffner effects the decomposition in two stages, using two similar vessels in succession. The first one being charged with liquor, just so much acid is added as suffices to decompose all the polysulphides present, whereby sulphur is precipitated and sulphuretted hydrogen evolved; this latter is allowed to escape. Next, sufficient hydrochloric acid is further added to decompose the thiosulphates present, and the liquor heated up by blowing in steam. More sulphur is thus precipitated, whilst sulphur dioxide escapes with the issuing steam. This is blown into the second vessel containing a second batch of liquor, when the sulphur dioxide decomposes the polysulphides, with precipitation of sulphur and formation mainly of thiosulphates. If the liquors are of the proper character, all polysulphides are thus decomposed by the time that all the sulphur dioxide has been expelled from the first vessel. The contents of the first vessel (chloride of calcium and sodium, sulphate of calcium, and suspended sulphur) are now discharged, and fresh liquor run into it; enough hydrochloric acid is now added to the second vessel to decompose all thiosulphates present and steam blown through, the escaping vapour passing into the first vessel, where they react as before. In this way the liquor in each vessel alternately is first subjected to the action of sulphurous acid, converting the polysulphides into thiosulphates with separation of sulphur, and then treated with hydrochloric acid, decomposing the thiosulphates, separating more sulphur, and liberating sulphur dioxide to pass into the other vessel and complete the cycle of operations. The precipitated sulphur is collected and fused by high-pressure steam as above described. According to Schaffner, when his instructions are properly carried out, no loss occurs by formation of trithionate and decomposition thereof into calcium sulphate &c.; but in actual practice considerable quantities of calcium sulphate are generally formed during the process, far more than could be accounted for by the small quantity of sulphuric acid present as an impurity in the hydrochloric acid used.

Apart from the value of the hydrochloric acid consumed (from 3½ to 4½ tons of acid sp.gr. 1·15 per ton of sulphur), both Mond's and Schaffner's processes have the disadvantage that even after several oxidations and lixiviations the quantity of brimstone actually obtained is far less than that contained in the waste. Very rarely is more than one half obtained under the most favourable conditions, whilst one-third, and sometimes considerably less, is more nearly the practical yield obtained in works where the process is carried out without very special arrangements as to skilled labour. Accordingly, whilst both methods have been somewhat extensively used, they yet leave a good deal to be desired so far as sulphur recovery is concerned, although what is obtained is gained with comparatively little expense.

Hofmann's process. A method based on somewhat the same chemical reactions as Mond's and Schaffner's methods has been introduced by A. P. Hofmann, and somewhat extensively worked at Dieuze (patented 1866). In this case the object was not only to utilise vat waste but also the 'still liquor' (acid solution of ferric and manganese chlorides) of the bleaching-powder works. A quantity of liquor is treated with vat waste in such proportion that a precipitate of sulphide of iron and manganese is formed, along with free sulphur, whilst neutral manganese and calcium chloride solution results. This solution is run off and the precipitate mixed with a large quantity of waste, and the whole formed into a heap and turned over with spades. Atmospheric oxidation quickly ensues, the iron and manganese sulphides acting as carriers, so that a large amount of polysulphide and oxidised sulphur compounds soluble in water rapidly forms, the heap heating considerably. After six or seven days the mass is lixiviated, and the undissolved portion again oxidised by exposure to air for three days and lixiviated. The residue left undissolved is now chiefly sulphate and carbonate of calcium, with oxides of iron and manganese, and is innocuous as regards odour and comparatively so as regards the drainage water issuing from it, whilst occupying much less bulk than the original vat waste. The liquors are then treated with fresh still liquor, when sulphur is precipitated by the three-fold action of the free acid on the polysulphides and thiosulphates present, of the free chlorine in solution on the sulphuretted hydrogen evolved, and of the ferric chloride present on the same gas; the proportion of the liquid resulting from the first lixiviation (containing most polysulphide), that from the second (containing most thiosulphate), and the still liquor, being so regulated that the resulting fluid is slightly acid with hydrochloric or sulphurous acid, or both, but does not contain sulphuretted hydrogen. The sulphur thus obtained is collected, and the manganese chloride solution freed from iron by treatment with a little more vat waste liquor, and, after clarification by subsidence, precipitated as manganese sulphide mixed with sulphur by yet more liquor. This precipitate after drying is roasted, whereby sulphur dioxide is evolved (used in the vitriol chamber), whilst a mixture of manganese sulphate and manganoso-manganic oxide is left. This is heated with sodium nitrate, whereby nitrous fumes are evolved (also used for vitriol-making), whilst sodium sulphate and peroxide of manganese result. These are separated by water, the peroxide being valuable for glass-making, containing no iron. Since the introduction of the Weldon manganese recovery system at Dieuze, this method has been disused.

Mactear's process. In all alkali works the heaps of vat waste accumulated during many years' working (save where the material is towed out to sea in lighters and there discharged) are a great source of inconvenience for many reasons, and more especially on account of the large bulk of 'yellow liquor' running from them in consequence of the conjoined effects of atmospheric oxidation and rainfall. At the St. Rollox works this evil was aggravated by springs of water, and the nuisance of the flow of the liquor into the adjacent brook and river became so great as to require abatement. Mactear's mode of treatment was primarily intended to deal with this inconvenience, so as to make it, if possible, a source of profit rather than the reverse; but the method generally is also applicable to solid vat waste, whether old or fresh, thereby leading to three slightly different modifications according to circumstances (Soc. Arts Journal, May 14, 1878). In one, the yellow drainage liquors from the vat waste heaps are mixed with a little lime and then treated with sulphurous acid, which is absorbed. On further adding hydrochloric acid, the temperature being 60-65°, decomposition takes place, precisely as with oxidised liquors prepared by Mond's process, little or no gas being evolved if the right proportion subsists between sulphides and oxidised sulphur compounds present. In another modification an aqueous solution of sulphurous acid is prepared by passing the gases from pyrites burners, or the combustion of waste sulphur &c., through a wooden scrubber filled with coke; this is then mixed with the yellow liquors to the proper extent, and the decomposition effected at 60-65° with hydrochloric acid as before. In the third modification, old waste already containing a good deal of calcium sulphite is ground up with water and treated with sulphurous acid until calcium bisulphite and precipitated sulphur are formed; or fresh waste may be similarly treated, whereby more free sulphur is produced. The calcium sulphite liquor is then mixed with yellow liquor in proper proportion and decomposed with hydrochloric acid as before. In these processes marketable brimstone is finally obtained, partly derived from the pyrites &c. used to produce the sulphurous acid, partly from the vat waste. Many thousands of tons of brimstone have thus been made at the St. Rollox works at a cost of about 61s. per ton. Obviously, however, if all alkali-makers obtained as brimstone not only all the sulphur in their vat waste, but also most of that in the pyrites used in Mactear's process (half as much again), the market price of such brimstone would fall so largely as greatly to diminish profits; whilst at present prices for pyrites sulphur, the latter would be far cheaper for vitriol manufacture than sulphur recovered at 3*l.* a ton.

Pechiney's process. Another method for dealing with vat waste drainage is that of Pechiney, whereby the yellow liquors naturally draining from the vat waste heaps are utilised for sulphur recovery by the simple process of blowing a stream of air and steam through the liquor in iron tanks by means of a Körting's injector until an amount of oxidation is effected just sufficient to prevent the evolution of either sulphuretted hydrogen or sulphur dioxide on addition of hydrochloric acid. The reactions here are substantially the same as in Mond's process, the main difference being that the oxidation is effected in a solution of polysulphides &c., instead of in the moist solid vat waste.[1] It has been suggested by W. Weldon (S. C. I. 1882, p. 47) that, instead of blowing and acidulating with hydrochloric acid, it would be cheaper to employ the solution of ferrous chloride resulting from copper extraction by the wet process to react on the vat waste drainage liquor, whereby sulphuretted hydrogen, free sulphur, and ferrous sulphide would be formed together with calcium chloride. By the action of ferric oxide the sulphuretted hydrogen could be converted into ferrous sulphide and sulphur; and, by exposing to air the ferrous sulphide mixed with sulphur thus obtained as a precipitate in either case, oxidation to ferric oxide and deposition of more sulphur would ensue, after which the sulphur could be burned off like that from the gas-purifier refuse of similar composition (*v. infra*). As yet, however, the process does not seem to have been tried on the large scale, the cost of carriage alone being prohibitive unless the ferrous chloride solution is close at hand to the vat waste liquor tank.

Schaffner and Helbig's process. Almost all the methods of sulphur recovery from vat waste above described have two important disadvantages. Firstly, hydrochloric acid is largely destroyed, thereby necessarily diminishing the possible output of bleaching powder, and to some extent increasing the difficulty experienced by Leblanc soda makers in competing with others using the ammonia process; secondly, the calcium carbonate used in the blackash process is not regained. In 1878 Schaffner and Helbig patented a process professing to remedy both these objections. This depended mainly on a remarkable reaction—viz. that of magnesium chloride—the action of which, on calcium sulphide, may be thus represented:

$$CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S.$$

The magnesia thence resulting is reconverted into chloride by treating the mass left after expulsion of sulphuretted hydrogen with gases rich in carbon dioxide, when the following change ensues:—$CaCl_2 + MgO + CO_2 = CaCO_3 + MgCl_2$. So that, ultimately, calcium carbonate (utilised for cement-making, the blackash process &c.) and sulphuretted hydrogen are the products, the latter being either used as a source of free sulphur or burnt to sulphur dioxide and converted into vitriol. The considerable degree of purity of the sulphuretted hydrogen thus obtained enables it to be thoroughly burnt with the formation of gases rich in sulphur dioxide and highly suitable for vitriol-making, and thus obviates many of the practical difficulties experienced by Gossage and others in employing sulphuretted hydrogen for this purpose, when prepared from vat waste by the action of furnace and limekiln gases, &c.[1] When used as a source of free sulphur, one-third of the sulphuretted hydrogen is burnt in ordinary coal-gas burners, and the products of combustion mixed with the other two-thirds and passed up a wooden tower or scrubber fed with a strong solution of calcium chloride. Under these circumstances the sulphur dioxide and sulphuretted hydrogen are stated by Schaffner and Helbig to react upon one another almost wholly in accordance with the equation

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[1] [illegible]

$$2H_2S + SO_2 = 2H_2O + 3S,$$

whilst in presence of water alone considerable quantities of polythionic (pentathionic, tetrathionic, and trithionic) acids are formed, according to Stingl and Morawski in virtue of the reactions

$$\begin{gathered}5H_2S + 5SO_2 = 4H_2O + 5S + H_2S_5O_6\\ 3H_2S + 4SO_2 = 2H_2O + 3S + H_2S_4O_6\\ H_2S + 3SO_2 = S + H_2S_3O_6,\end{gathered}$$

which circumstance, amongst others, prevented the successful use of the reaction of sulphur dioxide and sulphuretted hydrogen on one another by several previous inventors, notably Duclos (1839), Gossage (1859), and E. Bath (1862), the last-named employing almost exactly the same arrangements as Schaffner and Helbig, save that water instead of calcium chloride solution was sent down the reaction tower. The yield of sulphur from sulphuretted hydrogen, however, even when following Schaffner and Helbig's directions, always falls considerably short of that contained in the gas burnt, partly because some amount of polythionic acid is still produced, and partly because a portion of the sulphur is oxidised so as to form sulphuric acid, which is also lost; in practice, less than four-fifths of the sulphur only is usually regained in the form of brimstone.

During the years 1880-1883 A. M. Chance spent a considerable amount of time, labour and money in endeavouring to overcome various practical difficulties encountered successively in attempting to bring Schaffner and Helbig's process into successful manufacturing operation; his results are detailed in a series of papers (Journ. Soc. Arts, May 19, 1882, and S. C. I. 1882, 264; 1883, 202), and may be thus briefly summarised. The reaction of magnesium chloride on vat waste leads to a complete elimination of the sulphur present therein as oxysulphide in the form of sulphuretted hydrogen of considerable purity. By storing the gas in a gas-holder (containing water covered with a layer of 'dead oil' to avoid absorption) irregularities in supply can be obviated, and a steady current of gases of practically constant composition suitable for vitriol-making can be obtained by simply burning the gas in presence of a suitable excess of air (*v.* SULPHURIC ACID, p. 723). The chief practical difficulties which prevented Gossage from arriving at commercial success are thus obviated, and 90 or even 95 p.c. of the sulphur in the waste can be obtained in the form of chamber acid without any particular difficulty in working the plant, and with no unduly large consumption of nitre. On the other hand, not more than 75 to 80 p.c. of the sulphur is practically obtainable as brimstone, if that mode of utilising the sulphuretted hydrogen be adopted in accordance with Schaffner and Helbig's directions. As regards the regeneration of the magnesium chloride, by employing suitably-arranged decomposing vessels &c. and lime-kiln gases (at first containing 15 to 23 p.c. of carbon dioxide, but latterly, with improved arrangements, 28 or 29 p.c.), practically complete conversion of magnesia into magnesium chloride, and of calcium chloride into calcium carbonate, can be effected, and the mechanical loss during the separation of the last salt by filter presses can be reduced to small limits, whilst the addition of a little dolomite from time to time affords a supply of magnesium to compensate for losses. Sodium chloride is formed from the small amount of soda in the waste, but does not interfere with the chemical reactions; and when it accumulates to an undue extent after many repeated workings of the liquor, it can be readily removed by boiling down and 'salting out.' The calcium carbonate obtained might possibly be used for blackash making, but its suitability for this purpose is very doubtful; it is, however, by no means valueless, as it is well adapted for cement-making and analogous purposes. In fine, the cost of the process does not exceed an amount equivalent to a charge of threepence per unit of sulphur in Spanish pyrites (twelve shillings per ton at 48 p.c.). In the early part of 1883, when such pyrites cost twice as much, there was, therefore, a possibility of effecting a large economy in alkali-making by Leblanc's process by adopting this method of sulphur recovery; in view of which the pyrites companies speedily reduced their prices to something like threepence per unit, and effectually stopped the general adoption of the process by rendering it almost as cheap to purchase fresh sulphur in the form of pyrites as to erect and work the recovery plant.

Chance's process. As already stated, many attempts have been made by Gossage and others to utilise the sulphur of vat waste by decomposing the waste with carbon dioxide and burning the sulphuretted hydrogen evolved. The main cause of failure in all these earlier attempts was the irregularity in the composition of the combustible mixture of gases obtained which rendered all attempts to use them for vitriol-making practically impossible. This difficulty has been surmounted by Chance in a highly ingenious way (S. C. I. 1888, 162); firstly, guided by experience acquired in connection with Schaffner and Helbig's process (*v. supra*), improved lime-kilns were adopted capable of furnishing gases containing close upon 30 p.c. of carbon dioxide. Next, by employing a reaction well known in connection with gas purification, a great concentration of gas was effected: a series of vessels in succession was used containing the waste (made into a cream or slurry with water, and passed through a sieve to remove lumps); the limekiln gases were then passed through each vessel in the series successively, the following changes being produced: in the earlier vessels the entering carbon dioxide decomposes the waste in the well-known way, producing calcium carbonate and sulphuretted hydrogen; so that after traversing a certain mass of cream, practically all carbon dioxide is removed from the gases, which then consist essentially of a mixture of nitrogen and sulphuretted hydrogen. In the later vessels of the series, the sulphuretted hydrogen is *absorbed* by the waste, forming calcium sulphydrate, so that if the absorption is complete nothing but nitrogen escapes at the far end. The reaction here may be represented thus, regarding vat waste as calcium sulphide. $CaS + H_2S = CaH_2S_2$. Later on, when carbon dioxide reaches these vessels, owing to the earlier ones in the series having been worked off, the calcium sulphydrate thus formed is decomposed again, thus

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[1] Sulphuretted hydrogen produced as a by-product in certain chemical operations, such as the action of hydrochloric acid on galena, and stored in a gas-holder so as to enable an equable supply to be kept up, can be easily burnt so as to form gases suitable for vitriol-making, and has long been so employed. A convenient means of insuring regular combustion, especially with an intermittent supply, is to pass the gas into an ordinary pyrites kiln or smalls roaster (patented by P. A. Favre in 1855). The gases evolved in the manufacture of ammonium sulphate from gas liquors are sometimes thus treated (*v. supra*, p. 688).

$$CaH_2S_2 + H_2O + CO_2 = CaCO_3 + 2H_2S,$$

twice as much sulphuretted hydrogen being now evolved for a given amount of carbon dioxide in operation as is when carbon dioxide acts on fresh vat waste, thus

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S.$$

Accordingly, by working the operation in two stages, a gas much richer in sulphuretted hydrogen is obtained in one stage than could otherwise be secured, whilst during the other stage the sulphuretted hydrogen liberated is not collected but is absorbed by fresh waste, so that nitrogen passes off alone or nearly so. To effect this, a series of seven similar vessels is arranged with appropriate connections and cocks. During the first stage four only are in operation, the first and second being near exhaustion, whilst the third and fourth have been saturated with sulphuretted hydrogen during the previous stage, and are consequently giving off rich gas, which passes off to the sulphuretted hydrogen store gasometer. After a given period, Nos. 1 and 2 are quite exhausted and are discharged, the liquors after filtration not blackening lead salts; these are then re-filled and the series made up by taking in Nos. 5 and 6 (partially worked off previously, and standing idle during the first stage) and making Nos. 1 and 2 the last, No. 3 being thrown out of the series, so that the gases successively traverse Nos. 4, 5, 6, 7, 1, and 2. In Nos. 1 and 2 practically complete absorption of sulphuretted hydrogen takes place; but as a matter of precaution the residual nitrogen is passed through a lime or oxide of iron purifier. By and by the gases passing off from No. 6 become rich enough in sulphuretted hydrogen for collection. When this occurs, Nos. 1, 2, and 7 are thrown out of circuit, and No. 3 taken in, so that the gases now successively traverse Nos. 3, 4, 5, and 6. The same series of operations is now repeated, vessels Nos. 3, 4, 5, and 6 taking the place of Nos. 1, 2, 3, and 4 as at first; when Nos. 3 and 4 are exhausted they are discharged and re-filled, and the series made up again by discarding No. 5 and making the gases successively traverse Nos. 6, 7, 2, 3, and 4; and so on regularly, four vessels being always in circuit when sulphuretted hydrogen is collected for use, and six during the other stage when nitrogen escapes, the last two in this stage being the first two in the previous stage, re-filled with waste before coupling up again.

Operating in this way, a very considerable degree of constancy of composition of the gases stored in the gasometer can be attained, averaging close to 33 p.c. of sulphuretted hydrogen, between 1 and 2 p.c. of carbon dioxide, and 65 to 66 p.c. of nitrogen; in consequence of which the production of vitriol by burning the gases is rendered a very simple operation (*v.* SULPHURIC ACID, p. 723). By employing Claus' method (*v. supra*) of burning sulphuretted hydrogen in a limited supply of air in presence of ferric oxide as a carrier, either brimstone or flowers of sulphur are readily obtained, the yield being considerably greater than that attainable by Schaffner and Helbig's method. The cost of the process, whether brimstone or vitriol be made, was calculated in 1888 to be considerably less than that of the magnesium chloride process of Schaffner and Helbig; so that with a sulphur value of threepence per unit in pyrites, there was a large margin for economy in the process; whilst, on the other hand, in the event of a further fall in the price of pyrites sulphur, there would be the possibility of readily obtaining pure brimstone and flowers of sulphur from vat waste, and of competing successfully and profitably with Sicilian and other native sulphur supplies, even at prices considerably lower than those ruling in 1888.

Manufacture of brimstone and vitriol from sulphuretted hydrogen. Since the demonstration of the commercial practicability of obtaining sulphuretted hydrogen from vat waste by Chance's process, as above described, and converting this economically either into free sulphur (brimstone) or vitriol, according as market prices render the one or the other more profitable, a variety of processes and improvements have been brought forward, all more or less dependent on the same general ideas. Thus Chance has patented (S. C. I. 1889, 46) the production of sulphuretted hydrogen from gypsum by reducing it to calcium sulphide with carbon, and then treating it with limekiln gases; from 'yellow liquors' (drainage from alkali waste heaps) by similarly treating them (alone, or mixed with vat waste) with gases containing carbonic acid (S. C. I. 1889, 119); and from sulphides of sodium and potassium in similar fashion (S. C. I. 1889, 118); the sulphuretted hydrogen evolved from earlier vessels of a series being, in each case, absorbed in later ones, so as ultimately to obtain a much richer gas. Another patent for obtaining sulphuretted hydrogen from sodium sulphide by treatment with carbonic acid in a specially devised 'carbonator' was taken out in 1887 by J. B. Thompson (S. C. I. 1888, 626), the sulphuretted hydrogen being used either for brimstone-making or manufacturing vitriol. The same inventor has subsequently patented a process whereby sulphuretted hydrogen is reduced to sulphur by means of the fumes obtained by the decomposition of nitrates or of nitric acid, sufficient air being admitted to re-oxidise the nitric oxide formed, and so render the process continuous (S. C. I. 1889, 542). Hargreaves, Robinson, and Hargreaves have patented a process whereby sulphuretted hydrogen is obtained from vat waste by mixing with clay, forming into bricks, and heating by means of superheated steam; the residue, more strongly heated, forms cement (S. C. I. 1889, 118); also a special vessel wherein blackash is first lixiviated, and then the residual vat waste decomposed by carbonic acid, so as to produce sulphuretted hydrogen (*ibid.* 1890, 509).

Claus has patented a method for extracting brimstone from metallic sulphides by heating them with steam, highly superheated in stoves of the Whitwell type. Polysulphides lose sulphur, whilst neutral sulphides form sulphuretted hydrogen, by this treatment. By the regulated admission of air, the hydrogen of the sulphuretted hydrogen is burnt off, and the sulphur obtained in a series of condensing chambers (S. C. I. 1888, 440).

J. Hargreaves has patented an arrangement of perforated earthenware or metal blocks in a combustion chamber, into which a mixture of sulphuretted hydrogen is led, with just enough air to burn the hydrogen, the evolved sulphur being collected (S. C. I. 1889, 706) as with the Claus kiln.

Lyte and Tatters have patented a process for obtaining sulphur from sulphuretted hydrogen by mixing with a just sufficient quantity of air, and passing over magnesium chloride or oxychloride at 600–800°F. (315° to 425°C.); gaseous hydrochloric acid and sulphur are thus formed without the formation of sulphurous acid or the leaving unburnt any sulphuretted hydrogen. The sulphur is condensed, whilst the hydrochloric acid passes on and is otherwise utilised (S. C. I. 1890, 1,129).

Parnell and Simpson's process. A numerous series of patents has been taken out by Parnell and Simpson in connection with a process whereby sulphuretted hydrogen, suitable for brimstone or vitriol making, is obtained as one of the products along with soda ash (S. C. I. 1889, 11). Vat waste and ammonium chloride solution are heated together, with the result of producing ammonium sulphide and calcium chloride solution, the operation being performed in a series of four wrought-iron vessels so arranged that steam can be admitted into any one of them and passed through the remainder in series; the steam is always made to enter the one most nearly exhausted, and emerge from the one last refilled, so that the issuing vapours consist of ammonium sulphide with just enough steam to prevent the formation of solid crystals. These vapours are received in brine, ultimately forming a fluid containing per litre about 240 grms. of salt, and 65 of ammonia in the form of sulphide. Into this limekiln gases are passed, the liquid being contained in a series of eight carbonators, like those used in the Solvay process, provided with plates and mushrooms. These are worked in two sets of four each; in the first set the effect of the carbonic acid is indicated by the reaction

$$2(NH_4)_2S + CO_2 + H_2O = NH_4.H.CO_3 + NH_4.HS,$$

i.e. the carbonic acid is absorbed, whilst the nitrogen &c. mixed therewith passes off unmixed with any notable quantity of sulphuretted hydrogen. In the second set the contents have previously been treated with carbonic acid gas until practically the whole of the ammonium sulphide has been converted into bicarbonate and sulphydrate in accordance with the above equation; the effect of the carbonic acid is then to bring about the reaction:

$$NH_4.HS + CO_2 + H_2O = NH_4.H.CO_3 + H_2S,$$

so that sulphuretted hydrogen (mixed with nitrogen) escapes.

The connections are so changed in the progress of working that each carbonator, from the time it is charged as fresh liquor to the time it is finished, passes through the whole of the two series, beginning as the fourth of the first set, and then becoming in succession the third, second, and first; after which it is made successively the fourth, third, second, and first of the second set. Working thus methodically with kiln gas containing 30 p.c. of carbonic acid, a sulphuretted hydrogen mixture is obtained containing 25 p.c. of that gas on the average. This is led off and used for brimstone or vitriol making, as in Chance's process; the ammonium bicarbonate and salt react, as in the Solvay process, forming solid sodium bicarbonate and ammonium chloride solution, which is separated and worked up into sulphide with fresh vat waste. In order to regulate the due admixture of gas and air requisite for the combustion of sulphuretted hydrogen, a special mechanical arrangement is employed (Pat. 14,711, 1886).

The leading difficulty in working this process on the large scale seems to be that vat waste and ammonium chloride do not react so readily as to render the transformation into ammonium sulphide complete in a sufficiently short time.

Haddock and Leith's process. The formation of soluble calcium sulphydrate by the action of sulphuretted hydrogen on vat waste forms the first stage in this process (described at length S. C. I. 1891, 214); sodium sulphate is made to react on this, whereby calcium sulphate is precipitated, utilised as 'pearl hardener.' Through the sodium sulphydrate solution thus obtained limekiln gas is led, whereby sulphuretted hydrogen is evolved (made to react on a fresh batch of waste), and sodium bicarbonate formed. As only about one-half of the sulphuretted hydrogen thus obtained is required to form sulphydrate of calcium with the vat waste for the next batch, the other half is available for sulphur recovery. Of 100 parts of salt cake (produced from salt and sulphuric acid, with evolution of hydrochloric acid, available for bleaching powder), 56 are converted into blackash by the ordinary Leblanc process; the vat waste resulting from this enables the remaining 44 parts to be made into sodium bicarbonate by the sulphydrate process.

III. EXTRACTION OF SULPHUR FROM NATIVE SULPHATES.

A number of proposals have been made at different times to utilise the large stores of sulphur contained in mineral sulphates—*e.g.* gypsum—but hitherto these have not been carried out to any considerable commercial extent. For the most part they have been based on much the same principles as certain of the processes above referred to, whereby sulphur is indirectly extracted from sodium sulphate—*i.e.* by heating in contact with calcium carbonate and carbonaceous matter, conversion into calcium sulphide takes place, from which compound sulphuretted hydrogen is obtained by the action of acids or carbon dioxide: this sulphuretted hydrogen is then converted into vitriol by burning, or used as a source of sulphur.[1] In the manufacture of barium compounds from heavy spar (native barium sulphate), reduction to sulphide by heating with coal is the first step; the sulphuretted hydrogen thence obtained as a by-product has occasionally been utilised, but more with the object of getting rid of a noxious gas than with the view of profit; but with this exception little or nothing has ever been done beyond laboratory experiments with mineral sulphates, for the simple reason that vat waste is a far cheaper material to operate upon than any artificial sulphide formed by reduction of sulphate could possibly be. One of the more recent proposals in this direction is the patent of F. B. Rawes, No. 1,393, 1882, in which gypsum or old alkali waste is reduced to calcium sulphide by heating with carbon, this calcium sulphide, or fresh alkali waste, being then treated by a process analogous to that of A. M. Chance (*v. supra*, p. 694). C. R. A. W.

HYDRIDES OF SULPHUR.

Sulphuretted Hydrogen SH_2. This gas must have been known from very early times. It is described by the writers of the sixteenth and seventeenth centuries under the general name of 'sulphurous vapours.' Geber prepared milk of sulphur, but no mention is made of a fœtid-smelling gas being given off during the process. Scheele was the first, in 1777, to examine the gas minutely, and its chemical composition was definitely established by Berthollet.

Occurrence.—Sulphuretted hydrogen occurs among the gases issuing from volcanoes, sometimes to the extent of 25 p.c. of their volume. It is formed during the decomposition of animal substances, as blood, flesh, hair, &c. Decaying vegetable substances, particularly the leguminous plants, peas, beans, and lentils, when heaped together in a moist condition, evolve this gas. Sulphuretted hydrogen occurs in the hepatic waters of Harrogate, Aix-la-Chapelle, &c. Decomposing organic matter in contact with sulphates frequently generates the gas, and from this cause sulphides are occasionally found at the mouths of large rivers, which bring down much organic matter. The smell of sewer gas is in part due to this gas. The gas occurs in coal-gas, from which it has to be removed by a special arrangement in gas manufacture.

Preparation.—(1) It is best prepared by the action of dilute sulphuric acid upon ferrous sulphide: $FeS + SO_4H_2 = SO_4Fe + SH_2$. It should be collected over hot water, in which it is less soluble than in cold. The gas obtained by this method is never pure, as the sulphide used contains small particles of iron, which give rise to hydrogen. The gas should be washed in water to free it from acid or salt which may pass over. Excess of sulphuric acid causes a precipitate of white anhydrous ferrous sulphate, which coats the sulphide, and stops the evolution of gas.

(2) The pure gas is obtained by heating precipitated antimony sulphide with hydrochloric acid of sp.gr. 1·1: $Sb_2S_3 + 6HCl = 2SbCl_3 + 3SH_2$. If native sulphide of antimony be used, it should be first treated with hydrochloric acid to decompose any carbonates which may be present.

(3) The gas may be prepared on a large scale by heating a mixture of equal parts of sulphur and paraffin, aniline, or other organic bodies.

(4) By heating a damp mixture of sulphur and charcoal.

(5) Skey (C. N. 27, 161) proposes to substitute granulated zinc and native sulphide of lead for ferrous sulphide, acting on it with dilute hydrochloric acid (1 to 20). A rapid current of the gas can thus be obtained.

(6) Sulphuretted hydrogen is formed together with sulphur dioxide when steam is passed over boiling sulphur, or even when sulphur is boiled with water: $3S + 2OH_2 = 2SH_2 + SO_2$. The two gases thus obtained mutually decompose each other, so that only a portion of the sulphuretted hydrogen remains, and sulphur is deposited.

(7) By passing dry hydrogen over certain heated sulphides, as powdered antimony sulphide: $Sb_2S_3 + 3H_2 = Sb_2 + 3SH_2$. The gas is also formed by passing a current of hydrogen through boiling sulphur; by burning a jet of hydrogen in sulphur vapour, and by burning sulphur in an atmosphere of hydrogen.

Properties.—Sulphuretted hydrogen is a colourless, transparent, inflammable gas, possessing a most disagreeable smell resembling that of rotten eggs, which is due in part, when prepared from ferrous sulphide, to volatile sulpho-carbon compounds derived from the iron. It has a sp. gr. of 1·1912 (air = 1), and 1 litre at 0° and 760 mm. weighs 1·5475 grms. It burns with a pale-blue flame, forming water and sulphur dioxide, and depositing more or less sulphur:

$$SH_2 + 3O = SO_2 + OH_2$$
$$SO_2 + 2H_2S = 2H_2O + S_3.$$

A mixture of two volumes of sulphuretted hydrogen and three volumes of oxygen explodes violently when an electric spark is sent through it, complete combustion taking place.

The gas when inhaled acts as a powerful poison, producing asphyxia; even in small quantities it causes sickness and headache. According to Thénard, an atmosphere containing [illegible] its volume of this gas will kill a dog, and smaller animals die with even less than that amount. An atmosphere with $\frac{1}{250}$ is sufficient to kill a horse, while cold-blooded animals are not affected by this proportion of gas. The best antidote is the inhalation of very dilute chlorine, obtained by moistening a towel with dilute acetic acid, and sprinkling bleaching powder upon it.

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[1] Certain sulphates when [illegible] sulphur trioxide, or a [illegible] oxygen; this reaction was [illegible] earliest known [illegible] the name 'oil of vitriol.' Attempts to utilise the neutral sulphates of metals other than iron as sources of fuming acid have been made from time to time, but hitherto without much commercial success: alkaline acid sulphates, however, yield better results (*v.* SULPHURIC ACID, p. 713).

One volume of water at 0°C. dissolves 4·37 volumes of sulphuretted hydrogen, and at 15°C. 3·23 volumes. Its solubility at temperatures between 2° and 43·3° may be expressed by the formula: $c = 4{\cdot}3706 - 0{\cdot}083687t + 0{\cdot}0005213t_2$.

Alcohol dissolves at 0°C. 17·89 times its volume of sulphuretted hydrogen. The solution of sulphuretted hydrogen in water reddens blue litmus, whence the name hydrosulphuric acid, and possesses the peculiar smell and taste of the gas. The solution, however, soon decomposes, the hydrogen combining with oxygen, forming water, while sulphur deposits, giving to the liquid a milky appearance.

Sulphuretted hydrogen may be condensed to a colourless, mobile liquid, of sp. gr. 0·9 (water =1) under a pressure of seventeen atmospheres. The liquid boils at −61·8°, and freezes to an ice-like solid at −85°. It may be obtained in the liquid condition by cooling the gas in a tube to about −70° with a mixture of solid carbon dioxide and ether. It may also be liquefied by heating liquid hydrogen persulphide placed in one limb of a V-shaped tube. The compound undergoes spontaneous decomposition, with evolution of sulphuretted hydrogen and deposition of sulphur, the tension produced being sufficient to liquefy the sulphuretted hydrogen.

Sulphuric acid cannot be used for drying sulphuretted hydrogen, because it is decomposed by it: $SH_2 + SO_4H_2 = S + 2OH_2 + SO_2$. It is decomposed by nearly all oxidising agents into hydrogen and sulphur. Chlorine, bromine, and iodine appropriate its hydrogen, and sulphur is deposited:

$$SH_2 + Cl_2 = 2HCl + S\ ;\ SH_2 + I_2 = 2HI + S.$$

The latter reaction takes place only in presence of water. Fuming nitric acid dropped into a jar of the gas decomposes it with explosive violence. Sulphuretted hydrogen immediately tarnishes silver, hence silver egg spoons are frequently gilded, to prevent blackening when used in eating eggs. Silver coins carried in the pocket with lucifer matches become blackened from formation of silver sulphide. The surface of mercury becomes tarnished in contact with the gas. Potassium, when heated, burns in sulphuretted hydrogen, forming potassium sulphide. Lead oxide, in contact with the gas, yields lead sulphide and water: $PbO + SH_2 = PbS + OH_2$. Sulphuretted hydrogen generally converts metallic oxides into sulphides. Moist sulphuretted hydrogen mixed with air as oxygen is converted at from 40° to 90° into sulphuric acid. Paper impregnated with a solution of a soluble salt of lead, as lead acetate, is used as a test for this gas. Such paper is blackened in contact with sulphuretted hydrogen. For the same reason paintings containing white lead are darkened by exposure to the air of towns; cards glazed with white lead, and engravings on paper whitened with that substance, suffer similarly.

Sulphuretted hydrogen is decomposed by compounds rich in oxygen, *e.g.* ferric hydrate:

$$Fe_2(HO)_6 + 3SH_2 = 2FeS + S + 6OH_2.$$

This reaction is utilised on a large scale to remove sulphuretted hydrogen from coal-gas. Both as a gas and in solution sulphuretted hydrogen is largely employed in analytical operations. The sulphides of the metals have in many cases characteristic colours, by which many of them may be easily recognised in qualitative examinations of their salts; thus zinc sulphide is white, cadmium sulphide yellow, antimony sulphide orange, tin sulphide chocolate, and copper sulphide black.

A solution of the gas to be used as a reagent should be made with boiled water, or with water which has already been charged with the gas. By closing the bottle with a greased stopper, and inverting it with the neck standing in water, the solution may be preserved for weeks. A solution of the gas in glycerin keeps better, and is occasionally used as a reagent.

Sulphuretted hydrogen is easily decomposed when heated alone, as when the gas is passed through a red-hot tube. According to Myers (A. 159, 124), a temperature of 400° is sufficient to cause the decomposition. When tin is heated in the gas a sulphide is formed and hydrogen liberated, which occupies the same volume as the original gas. When a spiral of platinum is heated in the gas, sulphur is deposited and hydrogen is set free.

Uses.—Sulphuretted hydrogen is used on a large scale for removing arsenic from sulphuric acid, for precipitating copper from solutions of the salts of that metal, and for precipitating gold in the extraction of gold and silver, from waste material containing them, by the chlorine process.

Hydrogen persulphide H_2S_2 (?).

This compound was discovered by Scheele, and more completely investigated by Berthollet. It was first obtained by pouring a concentrated solution of penta-sulphide of potassium, K_2S_5, into dilute hydrochloric acid, when on standing some time yellow drops of a transparent oily liquid separated out. Berthollet believed it to be analogous in composition to the sulphide of potassium used in its preparation, and assigned to it the formula H_2S_5. Thénard, however, who found it possessed many properties in common with hydrogen peroxide, gave it the formula H_2S_2, although his analyses always showed a larger proportion of sulphur than is demanded by this formula. Hofmann, who obtained the compound by decomposing a crystalline compound (formed by the action of ammonium persulphide on strychnine) with hydrochloric acid, believed it to possess the formulæ H_2S_3. More recently Schmidt has shown that strychnine combines with sulphuretted hydrogen to form a crystalline body, but that it does so only in the presence of oxygen, thus:

$$2C_{21}H_{22}N_2O_2 + 6SH_2 + O_3 = \\ (2C_{21}H_{22}N_2O_2 + 3H_2S_2) + 3OH_2.$$

This compound, on treatment with an acid, yields hydrogen persulphide. Owing to the ease with which the compound undergoes decomposition into sulphuretted hydrogen and sulphur, and the solubility of the latter in hydrogen persulphide, it is almost impossible to obtain it pure, and its composition is based more upon its analogy with hydrogen peroxide than upon exact chemical analysis.

Preparation.—It is obtained by pouring a solution of calcic disulphide into an excess of cold concentrated hydrochloric acid, when the hydrogen persulphide separates out as a heavy yellowish oil: $CaS_2 + 2HCl = H_2S_2 + CaCl_2$. The calcium disulphide is prepared by boiling milk of lime with an excess of sulphur, and then filtering. The solution of disulphide should be poured into the acid, as the hydrogen persulphide is more stable in acids than in alkalis.

Properties.—Hydrogen persulphide is a heavy, yellowish, oily liquid, of sp.gr. 1·7342. Its odour resembles that of sulphuretted hydrogen, but is more pungent, and its vapour attacks the eyes. It has an acrid, unpleasant taste. It undergoes decomposition at ordinary temperatures into sulphuretted hydrogen and sulphur, the decomposition being greatly facilitated by elevation of temperature. It has been distilled at the reduced pressure 0·04–0·01m., and temperature 60°–85°, the distillate being of a bright pale-yellow colour, very limpid and mobile, with an extremely irritating odour (P. Sabatier, C. R. 100, 1346). It is easily soluble in carbon disulphide and ether, and insoluble in chloroform and benzene. It is inflammable, and burns with a blue flame. Like hydrogen peroxide, it bleaches organic colouring matters, and it reduces the oxides of gold and silver with so much energy as to cause ignition (Odling). Hydrogen persulphide dissolves phosphorus and iodine, gradually changing them into phosphorous sulphide and hydrochloric acid respectively. Sulphur dioxide has no action on it, in which respect it differs essentially from sulphuretted hydrogen. The liquid produces superficial whity eschars on the skin and mouth. Under the action of finely-divided platinum, gold, iridium, and charcoal, hydrogen persulphide, like hydrogen peroxide, undergoes instantaneous decomposition.

OXIDES AND OXYACIDS OF SULPHUR.

Sulphur dioxide SO_2.

The ancients knew that when sulphur was burnt it evolved pungent fumes. The fumes of burning sulphur have long been used for fumigation purposes, and for purifying cloth. It was for a long time thought that sulphuric acid was produced by burning sulphur in the air, but Stahl proved the fallacy of this idea; it was known by the name of phlogisticated vitriolic acid, in accordance with the views of that time. Priestley, in 1775, first prepared the pure gas.

Sulphur dioxide occurs among the gases issuing from volcanoes, and in a state of solution in the waters of certain volcanic springs. It also occurs to a small extent in the air of towns, being derived from the pyrites contained in coal.

Preparation.—1. By burning sulphur in air or oxygen. The sulphur ignites at a temperature of about 240–260°, and sulphur dioxide is obtained equal in volume to that of the oxygen consumed: $S + O_2 = SO_2$.

2. By roasting pyrites. This method is mainly employed in the manufacture of sulphuric acid on the large scale.

3. By heating a mixture of peroxide of manganese and sulphur: $MnO_2 + S_2 = MnS + SO_2$.

4. By the decomposition of sulphites, as sodium sulphite, with warm dilute sulphuric acid: $Na_2SO_3 + SO_4H_2 = Na_2SO_4 + OH_2 + SO_2$.

5. By heating a mixture of sulphur and sulphuric acid: $S + 2SO_4H_2 = 2OH_2 + 3SO_2$.

6. By the action of strong sulphuric acid upon such metals as copper, mercury, or silver, which do not evolve hydrogen on treatment with that acid:

$$Cu + 2SO_4H_2 = CuSO_4 + 2OH_2 + SO_2.$$

This is the method commonly employed for obtaining the gas for laboratory or lecture purposes.

7. By the action of sulphuric acid upon charcoal: $C + 2SO_4H_2 = 2OH_2 + CO_2 + 2SO_2$. This method is made use of on the large scale in the manufacture of the alkaline sulphites; carbon dioxide is evolved at the same time, but, for the purpose named, it is not detrimental, as carbon dioxide is almost insoluble in water containing sulphurous acid.

Sulphur dioxide may be produced from pyrites or other sulphur compounds by the apparatus shown in fig. 3. The sulphur is replaced by silica or other slag-producing material, and being thus set free is oxidised by a blast of hot or cold air. The small blast-furnace A is heated to a white heat, and then charged with a mixture of pyrites and sandstone, siliceous limestone, or other slag-producing material. A hot blast is then directed through the tuyères B, by which the mixture is reduced to the molten condition and the sulphur set free and carried upwards, together with some sulphur dioxide formed, while the silica combining with the iron forms a slag, and is run off from time to time. A hot blast of air is directed into the tubes C and D, which are lined with brick, in order to completely burn the sulphur. In connection with the pipe D is a water lute, E, which serves as a safety valve in the event of excessive pressure of the gas (Mathieson and Hawliczek, S. C. I. 6, 41).

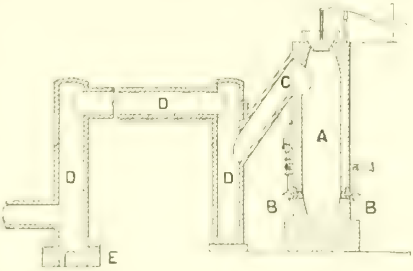

FIG. 3.

Schröder and Hänisch have patented a process for obtaining liquid anhydrous sulphurous acid from furnace gases containing only a small amount of sulphur dioxide. The gases are first conducted into cold water, the solution so obtained is heated to drive off the sulphur dioxide, and the condensation is effected by compression or refrigeration. The gases from the roasting-kiln are passed into an absorbing tower, filled with coke, and are met by a copious spray of water. The solution formed is collected in a series of closed pans made of sheet lead. The pans are then heated to expel the gas, which is dried by calcium chloride, and passes thence to a compression pump. The last traces of gas are removed from the water by allowing it to pass through a tower filled with lead-wire network, where it meets steam at the bottom. The pressure is regulated by means of a taffeta bag, and the gases compressed by the pump are cooled by a condensing worm, and pass into the receiver, whence the liquid sulphurous acid may be drawn off for use (S. C. I. 4, 674).

The apparatus here figured has been devised by Raoul Pictet for the manufacture of sulphur dioxide on a large scale. Sulphur dioxide is obtained from sulphur and sulphuric acid, and introduced into the inclined refrigerator B, 18 to 20 metres long. The pump D aspirates the gas through the tube C, and drives it forward to the condenser E, which consists of a system of tubes continually surrounded by a current of water. An unbroken stream of the liquefied gas flows through the tube F, regulated by the tap *h*, into the refrigerating tube B, cooled thereby to $-10°C.$ by means of alternate exhaustion and condensation. All hydrates of sulphurous acid are thus separated out in this tube in a crystalline form, and dehydration takes place. The dehydrated gaseous acid is drawn onwards by the pump and again liquefied, in order to once more return to the refrigerating tube. When the operation is continued slowly, the entire quantity of sulphurous acid prepared will have collected in the tube B. As soon as hoar-frost covers the whole tube, and it is evident that the quantity of acid is sufficiently great, the pump D is stopped, and the sulphur dioxide allowed to escape through the tube M in a gasometer (D. P. J. 249, 306).

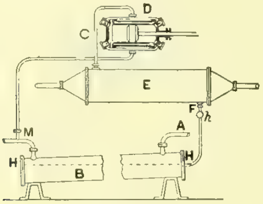

FIG. 4.

Properties.—Sulphur dioxide at ordinary temperatures is a colourless, irrespirable, incombustible gas, sp.gr. 2·22 (air = 1). It may be collected by downward displacement like carbon dioxide, but when required quite free from air it must be collected over mercury. It possesses the well-known odour of burning sulphur, is condensable to a liquid at the temperature obtained by a mixture of ice and salt, or by a pressure of about 2·5 atmospheres at ordinary temperatures; solid at $-76°C.$ Sulphurous acid gas is very soluble in water, the solution being attended with a slight elevation of temperature; at 0°C. water dissolves 79·789 times its volume of the gas, at 20°C. 39·374 volumes, and at 40°C. 18·766 volumes, prolonged ebullition being required to expel the last traces of the gas (Schoenfeld, A. 95, 2). The solution of the gas has a strong acid reaction, reddens blue litmus, and afterwards bleaches it, but the perfectly dry gas has not these properties. It is also soluble in concentrated sulphuric acid, that liquid taking up at ordinary temperatures fifty-eight times its volume of the gas. A saturated solution of the gas in water at 0°C. deposits a crystalline hydrate, $SO_4H_2,14H_2O$, which melts at a temperature of from 1° to 2° without evolution of gas. Sulphur dioxide, both as gas and in solution, possesses strong bleaching properties, and is used in bleaching such materials as are injured when bleached by chlorine: these properties were known to Paracelsus. The bleaching action of sulphur dioxide is a reducing one, while that of chlorine is an oxidising action; thus sulphur dioxide in presence of moisture is oxidised with formation of sulphuric acid, the liberated hydrogen forming a colourless body with the colouring matter: $SO_2 + 2OH_2 = H_2SO_4 + H_2$.

The colouring matters are probably in many cases not destroyed by the acid, but form with it colourless combinations, for in time the original colour often appears, as is the case with straw and flannel, which become yellow with age.

Chlorine and sulphur dioxide mixed in equal volumes and exposed to sunlight combine directly, forming a colourless liquid, sulphuryl chloride, possessing an irritating odour: $SO_2 + Cl_2 = SO_2Cl_2$.

Sulphur dioxide and sulphuretted hydrogen mutually decompose each other in presence of moisture with deposition of sulphur, formation of water, and pentathionic acid: $10SO_2 + 10SH_2 = 8OH_2 + 5S_2 + 2H_2S_5O_6$. When sulphur dioxide and oxygen are passed over heated spongy platinum the two gases combine with formation of the higher oxide of sulphur. Sulphurous acid gas combines with ammonia gas forming two solid compounds, $SO_2(NH_3)_2$ and $SO_2.NH_3$. Nascent hydrogen converts it into sulphuretted hydrogen. Potassium, when heated, burns in sulphur dioxide, forming thiosulphate and sulphite of potassium; tin and finely-divided iron are changed partly into sulphides and oxides when heated in the gas; when the gas is passed over metallic peroxides, as peroxide of lead, sulphates are formed: $PbO_2 + SO_2 = PbSO_4$. When acted upon by metallic hydrates, sulphurous acid produces sulphites: $SO_2 + OH_2 + OKH = SO_3HK + OH_2$. Arsenic, chromic, and permanganic acids are all reduced by sulphur dioxide, and gold is precipitated from its solutions by the gas or aqueous solution. At a temperature of about 1,200° sulphur dioxide is decomposed into sulphur and oxygen, part of the latter combining with a portion of the undecomposed sulphur dioxide to form the higher oxide; it cannot, however, be entirely decomposed in this way by electricity, unless the sulphuric anhydride as formed is absorbed by sulphuric acid. Tyndall has shown that the gas is also decomposed by passing a beam of sunlight through a long tube filled with the gas, when a white cloud is formed consisting of sulphur trioxide.

The composition of sulphur dioxide is ascertained by burning sulphur in a flask of oxygen inverted over mercury. The sulphur is placed in a cup inside the flask, and is so arranged that the sparks from an induction coil on passing between wire terminals come in contact with and ignite the sulphur; the volumes of oxygen before combustion, and of sulphur dioxide after combustion, are found to be the same. When a solution of sulphur dioxide is kept for some time in a bottle containing air, its smell gradually disappears, through absorption of oxygen, whereby it is converted into sulphuric acid.

Sulphur dioxide may be condensed in quantity by generating the gas in the usual way from copper and sulphuric acid, allowing the evolved gas to pass through a wash-bottle, and thence through a worm-tube surrounded by a freezing mixture of ice and salt, and terminating in the neck of a flask placed below, which is also surrounded by a freezing mixture; the drops of liquid sulphur dioxide accumulate in the flask, which is drawn out to a narrow point in the neck, at which point it may be hermetically sealed to preserve the liquid. It may also be obtained liquid by sealing in a thick glass tube a mixture of one part sulphur and five parts of sulphuric anhydride, when the following action occurs: $S + 2SO_3 = 3SO_2$. The contents of the tube acquire a blue colour, which in a few days disappears, the two solid substances having been transformed into a colourless liquid. The liquefaction by pressure may be effected as follows. A strong glass tube is sealed at one end, and then filled with the dry gas; a well greased, tightly-fitting caoutchouc stopper is then inserted into the tube, and forced into it by means of an iron rod till the volume of gas is reduced to about one-fifth its original bulk, when drops of liquid sulphur dioxide deposit in the tube.

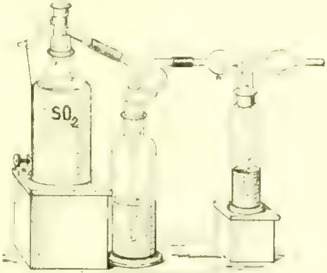

FIG. 5.

Liquid sulphur dioxide boils at −8° (Pierre, C. R. 70, 92), its vapour tension at 0° is 1·16506 metres of mercury, and its sp.gr. at −20·5° is 1·4911. It dissolves iodine, sulphur, phosphorus, resins, and many other substances which are insoluble in water. When it is poured into a small quantity of water, part is dissolved, whilst the greater portion is rapidly evolved, the temperature falling so low as to freeze the water. Mercury may also be frozen by covering a small quantity of it in a capsule with a deep layer of the dioxide, and then forcing a rapid current of air through the liquid. Chlorine and ammonia gases when passed through bulb-shaped tubes, surrounded by cotton-wool kept moist by liquid sulphur dioxide, are condensed to liquids. When the liquid dioxide is evaporated under the air-pump by quickly exhausting the receiver, so much heat is absorbed that it freezes to a snow-like mass. By cooling the liquid dioxide in a mixture of solid carbon dioxide in ether it solidifies to a transparent mass heavier than the liquid. The low temperature of −140°C. is obtained by the evaporation of solid carbon dioxide in liquid sulphur dioxide, and has been employed in the liquefaction of oxygen and nitrogen.

Detection.—For this purpose paper steeped in a solution of potassium iodate and starch is brought into the gas, which is at once turned blue by formation of iodide of starch. In this way mere traces of the gas may be detected:

$$2KIO_3 + 5SO_2 + 4OH_2 = I_2 + 2HKSO_4 + 3SO_4H_2.$$

When the sulphur dioxide is in excess, the blue paper is again bleached and hydriodic acid formed: $I_2 + SO_2 + 2OH_2 = 2HI + SO_4H_2$. The last reaction has been turned to account in estimating the amount of sulphur dioxide in solution. A small quantity of starch paste is added to the solution, and then standard iodine solution is introduced from a burette until a permanent blue colour from the formation of iodide of starch is obtained. The solutions for this purpose should be dilute, as sulphuric and hydriodic acids mutually decompose each other; thus $2HI + SO_4H_2 = I_2 + H_2SO_3 + OH_2$. Bunsen has shown that when not more than 0·05 p.c. of sulphurous anhydride is present the last reaction disappears, and the reduction of iodine to hydriodic acid is complete, and upon this reaction he has founded a method for the quantitative determination of iodine, and indirectly of many other substances (A. 86, 265).

Uses.—Sulphur dioxide has now many useful applications in the arts and manufactures, foremost among which is its use to the vitriol manufacturer; enormous quantities of the gas are produced for this purpose, chiefly from pyrites. It is used by the paper-maker in the manufacture of wood pulp and to remove the last traces of chlorine after bleaching the pulp:

$$SO_2 + Cl_2 + 2OH_2 = H_2SO_4 + 2HCl.$$

The tanner uses it for softening dry hides and skins in the bath or 'soak,' which is composed of solution of sulphurous acid, and in the 'puring' operation for the purpose of curtailing or dispensing with the use of animal excrement. Sulphurous acid is also contained in the tanning liquor in the process of tanning (S. C. I. 2, 288). It has been used with advantage in the treatment of fur, wool, hair, and other feltable material so as to facilitate the felting of these materials (S. C. I. 5, 378). Sulphur dioxide is used in the manufacture of borax. It is also employed in refining sugar, 1 p.c. of a solution of 8–10 p.c. strength is added to the crude juice, and the insoluble substances produced are filtered off. In decolourising the gas is used. When employed in the first case it is possible to diminish the amount of lime used without reducing the purity of the product. The acid produces glucose in beet-juice only after long exposure to the air (L. Battut, C. C. 1884, 854). It is a convenient means of removing stains of fruit and port wine from linen. Messrs. Du Molay & Rossi in 1880 adopted it for producing ice, and a mixture of liquid carbon dioxide and sulphur dioxide is known as 'Pictet's liquid' (S. C. I. 5, 139).

Sulphur dioxide is a powerful antiseptic, and has been successfully employed in preserving meat and stopping fermentation, fumigating clothes, and disinfecting the air of rooms. It is used for killing mould in wine and beer casks. Instead of burning sulphur for disinfecting purposes, in which there is some danger of fire, Messrs. Boake & Co. have patented a process which consists in storing the liquid dioxide in a closed vessel, and when required for use opening the same by means of a lever attached to a screw, by which means a stream of almost any desired rate can be obtained by regulating the screw. The flow may be continued for as much as forty hours, and a single siphon will evolve 500 litres of sulphurous acid gas (Patent 12,238, 1885).

Liquefied sulphurous anhydride was exhibited by Messrs. Boake & Co. at the International Inventions Exhibition in copper drums, containing 1 and 2 cwts. respectively.

Sulphur dioxide is used in preference to chlorine in bleaching silk, straw, wool, sponge, isinglass, baskets, &c., because the latter injures these materials in the bleaching process. The objects may be treated either by the gas or the solution, the latter being least effective. The goods after washing and wringing are brought, while still damp, into a closed chamber and covered with a thick cloth. They are then exposed to the action of sulphur dioxide produced by burning sulphur in a chauffer placed on the floor of the chamber, and are left for 12–24 hours, according to the whiteness required. The goods are then washed in lukewarm dilute hydrochloric acid to remove particles of adhering sulphur deposited thereon. For bleaching loose wool, a solution of bisulphite of soda is preferably used, the substance being afterwards passed through lukewarm dilute hydrochloric acid, whereby sulphur dioxide is evolved in the nascent condition and bleaches the wool (D. P. J. 245, 183).

Sulphurous acid has been used recently to a considerable extent in Germany for the purpose of giving to old barley the fine yellow colour of the new grain, and the buyer may easily be deceived by the appearance. Such treatment is injurious to the germinating power, and may be detected by steeping the barley in hot water for a quarter of an hour, then adding zinc and hydrochloric acid to the aqueous extract, the presence of sulphur being indicated by the evolution of hydrogen sulphide (H. Eckenroth, Z. 11, 110).

Sulphur dioxide is an effective agent for extinguishing burning chimneys; the sulphur being thrown on the fire ignites, and the gaseous product suffocates the flame.

Sulphur dioxide is employed in the treatment of cutaneous diseases. The patient is placed in a box provided with an aperture at the top, through which his head passes, and a wet cloth around his neck prevents the escape of gas from within. The box is over a small fireplace in which sulphur is burned, so that the patient sits in an atmosphere of sulphur dioxide.

Sulphurous acid H_2SO_3.

This acid is only known in solution. It smells and tastes like the gas, and has a strong acid reaction. It is dibasic, and forms two series of salts, termed 'sulphites.' The two series of salts are termed 'acid' and 'normal' sulphites respectively. The following are types of these different salts:—

Acid Sulphites	Normal Sulphites
SO_3NaH	SO_3Na_2
SO_3KH	SO_3Ca
SO_3AgH	SO_3K_2

The sulphites of the alkali metals are easily soluble in water, the normal sulphites of the other metals being almost or quite insoluble in water. They dissolve in aqueous sulphurous acid, however, with formation of the acid sulphites, but are again decomposed on evaporation, with evolution of sulphur dioxide and formation of the normal salts. They have no odour, those dissolving in water possessing a sharp taste. They are easily detected by addition of sulphuric acid, when they give off the smell of burning sulphur. Their neutral solutions give a precipitate with barium chloride which is soluble in hydrochloric acid; on the other hand, if nitric acid be added to the solution and warmed, a precipitate of sulphate of barium is obtained.

Hyposulphurous acid H_2SO_2. Berthollet, in 1789, observed that iron dissolved in aqueous solution of sulphur dioxide without evolution of gas, and Fourcroy and Vauquelin found, in 1798, that tin and zinc act similarly. The nature of this action was first traced by Schützenberger, to whom the credit of the discovery of hyposulphurous acid is due (C. R. 69, 169).

Preparation.—It is obtained by dissolving zinc or iron in a strong aqueous solution of sulphurous acid: $H_2SO_3 + Zn = ZnO + H_2SO_2$. No oxygen is evolved, and as the metal dissolves the solution acquires a yellow colour. It is a more powerful bleaching agent than sulphurous acid, requiring an atom of oxygen more than the sulphurous acid to convert it into sulphuric acid, thus:

$$H_2SO_2 + O_2 = H_2SO_4$$
$$H_2SO_3 + O = H_2SO_4.$$

It is a powerful reducing agent, precipitating mercury and silver from solutions of their salts:

$$HgCl_2 + SO_2H_2 + OH_2 = H_2SO_3 + 2HCl + Hg.$$

The best way to prepare it is to immerse zinc chips in a strong solution of acid sodium sulphite, when the zinc quickly dissolves, forming zinc sodium sulphite, $Na_2Zn(SO_3)_2$, which separates out. The supernatant liquid is decanted into a flask, well corked, and kept cool, then three or four times its volume of alcohol is added, which causes the remainder of the zinc sodium sulphite to separate out, giving a second crop of crystals. The clear liquid is then poured off into a smaller flask till quite full, and is then well corked. The liquid soon becomes a semi-solid mass of colourless needles of sodium hyposulphite, $NaHSO_2$. This is an unstable compound, quickly absorbing oxygen from the air, and is converted into sodium hydrogen sulphite, $NaHSO_3$; even when not exposed to air, it decomposes thus: $2NaHSO_2 = OH_2 + Na_2S_2O_3$.

Hyposulphite of soda is also formed by passing a current of electricity through acid sodium sulphite, the evolved hydrogen abstracting an atom of oxygen from the salt, and forming water.

The solution of sodium hyposulphite is used by the dyer and calico printer for the reduction of indigo, as it possesses the same bleaching properties as the free acid.

A solution of the free acid is obtained by decomposing the aqueous solution of the salt with oxalic acid. The solution so obtained has an orange colour, bleaches strongly, and rapidly decomposes on exposure to the air from the absorption of oxygen.

Sugar juice is decolourised by hyposulphurous acid or its salts, preferably by the salts of aluminium, zinc, iron, &c. Two to three parts of one of the salts suffice for the treatment of 1,000 parts of the juice. By this process a pure syrup of exceptionally high density is obtained (S. C. I. 6, 47).

Dithionic acid $H_2S_2O_6$. Formerly called hyposulphuric acid. Discovered by Welter and Gay-Lussac in 1819. The manganese salt of this acid is obtained by passing a stream of sulphur dioxide through water containing finely-divided manganese dioxide in suspension, the liquid being kept cool: $2SO_2 + MnO_2 = MnS_2O_6$. The manganous sulphate formed at the same time is removed by addition of barium hydrate, which precipitates insoluble manganous hydrate and barium sulphate, which are filtered off. By cautiously adding dilute sulphuric acid to the clear solution until no more precipitate forms, and then filtering off the barium sulphate, a solution of dithionic acid remains. This solution may be concentrated *in vacuo* until it attains a density of 1·347, when it is an inodorous and strongly acid liquid, easily decomposed into sulphuric acid and sulphur dioxide: $H_2S_2O_6 = SO_4H_2 + SO_2$. The acid solution in contact with air is gradually oxidised to sulphuric acid. The dithionates may be obtained by decomposing the barium salt by the sulphate of the corresponding base, or more simply by adding a soluble sulphate to barium dithionate. All the salts are soluble in water, and may generally be obtained in well-defined crystals, which are permanent in the air, and which, with the exception of the potassium salt, contain water of crystallisation. Their solutions mixed with hydrochloric acid and heated are decomposed, forming sulphur dioxide and sulphuric acid, without deposition of sulphur. Their aqueous solutions are not oxidised in the cold by either atmospheric oxygen, nitric acid, or potassic permanganate, but when heated with these they are converted into sulphates. On heating at 100° they undergo partial decomposition, and at a still higher temperature they are entirely decomposed, forming sulphur dioxide and a sulphate.

Thiosulphuric acid $H_2S_2O_3$, or $\left.\begin{matrix}HS\\HO\end{matrix}\right\}SO_2$, may be regarded as sulphuric acid in which half the hydroxyl has been replaced by an equivalent of sulphydryl, HS, and may be obtained by the sulphuration of sulphurous acid in the same way that the oxidation of the latter produces sulphuric acid. It cannot be preserved in the free state.

The thiosulphates may be obtained by digesting sulphur with solutions of the sulphites: $Na_2SO_3 + S = Na_2S_2O_3$, or by boiling sulphur with an alkaline hydrate:

$$3Ca(HO)_2 + S_{12} = CaS_2O_3 + 2CaS_5 + 3OH_2.$$

On exposing the deep-coloured solution to the air sulphur deposits, and a further quantity of thiosulphate is formed: $CaS_5 + O_3 = CaS_2O_3 + S_3$. The sodium salt was first prepared by Chaussier in 1799, and more thoroughly studied afterwards by Vauquelin. On adding hydrochloric acid to a solution of the salt the thiosulphuric acid is liberated, but is quickly resolved into sulphur and sulphurous acid. The soluble salts of thiosulphuric acid are also recognised by the facility with which they dissolve silver chloride, forming the double thiosulphate of sodium and silver, the solution of which has an intensely sweet taste: $AgCl + Na_2S_2O_3 = NaCl + NaAgS_2O_3$. A solution of mercurous nitrate is decomposed by a soluble thiosulphate, the black mercuric sulphide being at once deposited. When a thiosulphate is mixed with iodine solution an iodide and a tetrathionate are simultaneously formed. When the thiosulphates are heated with a solution of a cupric salt acidulated with hydrochloric acid they give a brown precipitate of cupric sulphide. Solutions of nickel and cobalt give, with the thiosulphates, dense black precipitates. Small traces of these salts may be detected by the red colouration given by the addition of a ruthenium salt made alkaline with ammonia. Treated with zinc and hydrochloric acid, the thiosulphates evolve sulphuretted hydrogen and deposit free sulphur.

Trithionic acid $H_2S_3O_6$. This compound was discovered by Langlois in 1842, who obtained the potassium salt by gently heating a solution of acid potassium sulphite with sulphur:

$$S_2 + 6KHSO_3 = 2K_2S_3O_6 + K_2S_2O_3 + 3OH_2.$$

The reaction probably occurs in two stages, in the first of which the thiosulphate is formed, and this is converted into the trithionate by the action of sulphur dioxide. This view is supported by the fact that the potassium trithionate can be obtained by acting on potassium thiosulphate with sulphur dioxide:

$$3SO_2 + 2K_2S_2O_3 = 2K_2S_3O_6 + S.$$

The free acid is obtained by adding fluosilicic acid to a solution of the potassium salt, when the insoluble fluosilicate of potassium is precipitated, and trithionic acid is set free, and has been obtained in prismatic crystals. The acid is stable in dilute solution, but when concentrated, even *in vacuo*, it readily undergoes decomposition into sulphur, sulphur dioxide, and sulphuric acid: $H_2S_3O_6 = S + SO_2 + SO_4H_2$. It has no smell, but has a strong acid and bitter taste. The only well-known salt is that of potassium, and this on heating undergoes decomposition into sulphur, sulphur dioxide, and sulphate of the metal.

The potassium salt is formed when potassium silver thiosulphate is heated with water, and the sodium salt when iodine is added to a solution of sodium thiosulphate and sodium sulphite: $Na_2S_2O_3 + Na_2SO_3 + I_2 = Na_2S_3O_6 + 2NaI$. A solution of a trithionate, treated with sodium amalgam, decomposes into sulphite and thiosulphate.

Solutions of the trithionates give black precipitates with mercurous nitrate, and white with mercuric nitrate. With silver nitrate they give a yellow precipitate, which soon becomes black. The solutions of the salts on heating are decomposed into sulphur dioxide, sulphur, and a sulphate.

Tetrathionic acid $H_2S_4O_6$. This acid was discovered in 1843 by Fordos and Gélis, who also prepared certain of its salts. They obtained the sodium salt by adding iodine to an aqueous solution of sodium thiosulphate. The barium salt is prepared by suspending barium thiosulphate in a small quantity of water, and adding iodine in small quantities at a time. Barium tetrathionate is separated in hydrated crystals, which contain two molecules of water:

$$2BaS_2O_3 + I_2 + 2OH_2 = BaSO_4O_6.2OH_2 + BaI_2.$$

When the reaction is complete the semi-solid mass is treated with alcohol, which dissolves the barium iodide and excess of iodine. The barium tetrathionate which remains may be purified by recrystallisation from a small quantity of water. The free acid is obtained by decomposing the barium salt with an equivalent quantity of sulphuric acid. The acid has a strong acid taste, is inodorous, and colourless. It is only stable in dilute solution out of contact with air, and may be concentrated *in vacuo* over sulphuric acid. On boiling the solution it decomposes into sulphur dioxide, sulphur, and sulphuric acid. The potassium salt is distinguished from the corresponding salts of the other polythionic acids by its action with sulphide of potassium, which converts it into potassium thiosulphate, with separation of sulphur:

$$K_2S_4O_6 + K_2S = 2K_2S_2O_3 + S.$$

Pentathionic acid $H_2S_5O_6$ or $S_3(SO_2OH)_2$ (Bloomstrand). On passing a slow stream of sulphuretted hydrogen into a nearly saturated aqueous solution of sulphurous acid the milky liquid is found to contain (*a*) small drops of sulphur in suspension, (*b*) sulphur in solution in the colloidal condition, similar to silica dissolved in dilute hydrochloric acid, (*c*) sulphuric acid, (*d*) trace of trithionic acid, (*e*) tetrathionic acid, (*f*) pentathionic acid, and (*g*) a polythionic acid, containing more sulphur than pentathionic acid, probably hexathionic acid (Debus, C. J. 1888, 53, 279). The clear solution can be concentrated on a water-bath without decomposition until it has sp.gr. 1·32, and *in vacuo* over caustic potash until sp.gr. 1·46, when it consists mainly of pentathionic acid (Wackenroder, Ar. Ph. 48, 272, 140; Kessler, P. 74, 249; Takatmatsu and Smith, C. J. 37, 592; 41, 162; Lewes, C. J. 39, 68; 41, 300). On adding, with constant stirring, to the concentrated solution about half the quantity of caustic potash which is required for complete neutralisation in dilute solution, and filtering from any precipitated sulphur, the clear liquid gives, by spontaneous evaporation, well-defined crystals of *potassium pentathionate*, $2K_2S_5O_6.3H_2O$ (Lewes). This salt can only be recrystallised from solutions containing a small quantity of free sulphuric acid; in presence of alkalis it is at once decomposed. A better method of obtaining the salt consists in adding potassium acetate, instead of caustic potash, to the concentrated solution. It dissolves in about 2 parts of water, forming a clear and neutral solution, insoluble in alcohol. The aqueous solution cannot be kept long without change; after a few days sulphur separates and potassium tetrathionate is gradually formed, $K_2S_5O_6 = K_2S_4O_6 + S$. The salt when heated is thus decomposed:

$$2K_2S_5O_6.3H_2O = 2K_2SO_4 + 2SO_2 + S_6 + 3H_2O.$$

On treatment with sulphuretted hydrogen pentathionic acid is decomposed as follows: $H_2S_5O_6 + 5H_2S = 10S + 6H_2O$. A solution of potassium pentathionate yields sulphur, potassium trithionate, and potassium thiosulphate:

$$3K_2S_5O_6 + 3H_2S = K_2S_2O_3 + 2K_2S_3O_6 + 3H_2O + 10S.$$

With bromine water it gives:

$$2K_2S_5O_6.3H_2O + 8Br_2 + 9H_2O =$$
$$4KBr + 4S + 6H_2SO_4 + 12HBr.$$

The pentathionates, with the exception of the potassium salt, have been but slightly examined. The copper salt, $CuS_5O_6.4H_2O$, forms small blue crystals, easily soluble in water (Debus).

The following are characteristic reactions for these salts:—

1. An ammoniacal solution of silver nitrate causes in a solution of potassium, ammonium, or barium pentathionate a brown colouration, which rapidly becomes darker, and by degrees a black precipitate is thrown down from the mixture. This reaction is not produced in a solution of tri- or tetrathionates, potassium thiosulphate, or ammonium sulphite. An ammoniacal solution of silver nitrate in fact seems to have no effect on them. Consequently, a pentathionate, even if present in very small quantity, can be detected by means of this reaction in a mixture containing potassium tri- and tetrathionates and sodium, potassium, or ammonium thiosulphates.

The solution of zinc in sulphurous acid produces, with an ammoniacal solution of silver nitrate, an immediate grey precipitate, and the supernatant liquid appears clear and colourless.

2. Potassium hydroxide, in solutions of pentathionates, immediately produces a separation of sulphur. As tri- and tetra-thionates and thiosulphates are not changed by this reagent, a proportionately small quantity of a pentathionate can be detected in a mixture of the four salts by addition of potassium hydroxide. The latter, however, is not so sensitive a reagent as the ammoniacal silver solution.

3. Ammonia added to a solution of potassium pentathionate causes, after about *one or two* minutes, a precipitation of sulphur.

4. Sulphuretted hydrogen produces, in an ammoniacal solution of a pentathionate, an immediate precipitate of sulphur.

5. An ammoniacal solution of mercuric cyanide produces with potassium pentathionate a black precipitate, by degrees at ordinary temperatures, at once at 100°C.

6. Ferric chloride, lead nitrate, cupric chloride, cupric acetate, cobalt nitrate, zinc sulphate, copper sulphate, lead acetate, hydrochloric acid, and barium chloride cause no change in solutions of potassium pentathionate (Debus, *l.c.*).

See also Plessy, C. R. 21, 473; A. Ch. 20, 162; Thomson, Ann. Phil. 12, 441; Lenoir, A. 62, 253; Ludwig, A. Ph. 51, 259; Fordos and Gélis, A. Ch. 22, 66, 28, 451; Sombrero and Selmi, A. Ch. 28, 210; Rister-Bennet, P. 116, 470; Chancel and Diacon, C. R. 56, 710; Rammelsberg, J. 10, 136; W. Spring, B. 6, 1,108; A. 199, 97; 213, 329; Stingl and Morawski, J. 1879, 1110; Curtius, J. pr. [27] 24, 225; Shaw, C. J. 43, 351; Smith, C. J. 43, 355; Salzer, B. 1886, 1696.

Hexathionic acid $H_2S_6O_6$. The probable existence of the potassium salt of this acid in the mother-liquor obtained by concentrating Wackenroder's solution, *i.e.* the product obtained by the mutual action of sulphur dioxide and sulphuretted hydrogen, has been indicated by Debus (C. J. [1888] 53, 278). It separates from its aqueous solution in warty masses without crystalline structure; its solution gradually decomposes, with separation of sulphur, even in presence of dilute sulphuric acid. Ammonia produces an immediate precipitate of sulphur (difference from pentathionate), and ammoniacal solution of silver nitrate reacts with hexathionate as with pentathionate (Debus).

General Reactions of Polythionates and Thiosulphates.

1. Mercurous nitrate produces with penta- and tetra-thionates a fine yellow precipitate, and with trithionates and thiosulphates a black precipitate.

2. Cupric sulphate mixed with solutions of potassium tri-, tetra-, or penta-thionates, or an aqueous solution of sulphurous acid, or the solution of zinc in sulphurous acid, causes no apparent change at common temperatures.

The same reagent does not affect tetra- and penta-thionates at 100°, but produces at this higher temperature with trithionates or thiosulphates a black, and with the solution of zinc in sulphurous acid a red, precipitate.

Copper sulphate added to a solution of ammonium sulphite produces a yellow precipitate at common temperatures.

3. Hydrochloric acid does not change solutions of tetra- and penta-thionates, but in about ten minutes in such as contain trithionates, and in about one minute in those of thiosulphates, it causes a separation of sulphur and sulphurous acid. A mixture of the four salts became turbid in two minutes.

4. Ferric chloride causes transient colouration in the following solutions:—

a. Thiosulphates, violet changing to yellow.

b. Sulphurous acid in water, brown changing to yellow.

c. Zinc in aqueous sulphurous acid, brown changing to colourless.

The reagent causes a permanent brown colour in aqueous solution of ammonium sulphite.

5. Barium chloride produces in solutions of sodium and potassium thiosulphate a white, crystalline precipitate which, even in boiling water, is only sparingly soluble, but it does not change solutions of the poly-thionates at common temperatures, or those of tetra- and penta-thionates at 100°. Thiosulphates and trithionates can be detected in a mixture of the two in the following manner:—Barium chloride is added to the neutral mixture as long as a precipitate is formed; the latter is barium thiosulphate, and can be proved to be so by means of ferric chloride and hydrochloric acid respectively. The filtrate from the barium thiosulphate is boiled for about five minutes, when, if barium trithionate is present, the smell of sulphurous acid will be perceived, and a white precipitate will be thrown down, insoluble in hydrochloric acid, and not volatile at a red heat on a piece of platinum-foil.

These reactions are not observed with barium dithionate.

If free acid should happen to be present in the original mixture, it must be neutralised with barium carbonate (Debus, *l.c.*).

Takamatsu and Smith (C. J. 37, 608) give the following table of reactions to distinguish tetra- and penta-thionic acids from each other, and from the other thionic acids:—

Reagents	Dithionic acid, $H_2S_2O_6$	Trithionic acid, $H_2S_3O_6$	Tetrathionic acid, $H_2S_4O_6$	Pentathionic acid, $H_2S_5O_6$
Caustic potash . .	No precipitate	No precipitate	No precipitate	Immediate precipitate of sulphur, re-dissolving gradually on standing, if not in much excess and coagulated.
Dilute hydrochloric acid	No action . .	Evolution of SO_2 and precipitate of S.	No action	No action.
Mercurous nitrate .	No precipitate	Immediate black precipitate, becoming white on standing.	Yellow precipitate, gradually darkening.	At first a yellow precipitate, turning white with excess of reagent on standing.
Silver nitrate . .	No precipitate	Yellow precipitate, soon becoming black.	Yellow precipitate, soon turning black, and also on adding ammonia.	Yellow precipitate, gradually darkening: black on adding ammonia.
Ammoniacal silver nitrate	—	No brown colouration, even on standing. On warming, Ag_2S formed.	No dark or brown colouration, even on standing, unless warmed.	Almost immediate brown colouration, becoming black on warming.
Mercuric cyanide .	No precipitate	—	At first yellow precipitate; gradually turning black on heating, with evolution of HCN.	At first yellow precipitate, gradually turning black on heating, with evolution of HCN.
Mercuric chloride .	No precipitate	Yellow precipitate, becoming white with excess of reagent.	On warming, white precipitate.	On warming, [illegible] precipitate.
Potassium sulphydrate solution.	—		White precipitate of sulphur.	White precipitate of sulphur.
Dilute solution of potassium permanganate	One drop, immediate black precipitate	One drop, immediate brown precipitate, even in presence of dilute SO_4H_2.	Decolourised, without addition of dilute H_2SO_4.	Decolourised, without addition of dilute H_2SO_4.

COMPOUNDS OF SULPHUR AND THE HALOGENS.

Sulphur and chlorine combine together to form three chlorides, viz. sulphur monochloride, S_2Cl_2; sulphur dichloride, SCl_2; and sulphur tetrachloride, SCl_4. Sulphur and chlorine gradually combine at ordinary temperatures, but the combination is greatly facilitated by heat.

Sulphur monochloride or **Sulphothionyl chloride** S_2Cl_2 was first obtained by Hagemann in 1781, but its composition was not fully established till the year 1810, when it was studied by Davy and Bucholz.

Preparation.—Sulphur monochloride is prepared by passing dry chlorine gas over melted sulphur, and distilling off the chloride from the excess of sulphur. The chlorine is generated in the ordinary way, and passed through a wash bottle containing water, then through calcium chloride, and thence to a retort containing melted sulphur. The chloride is condensed in a receiver cooled by a stream of cold water.

Properties.—Sulphur monochloride is an amber-coloured liquid, fumes strongly in air, and possesses a penetrating smell. Its sp.gr. is 1·70941 $\frac{0}{4}$ (Thorpe), and b.p. 138·1 (Thorpe). Water gradually decomposes it into sulphur, hydrochloric acid, and thiosulphuric acid, the last-named substance being afterwards decomposed into sulphur and sulphurous acid:

$$2S_2Cl_2 + 3OH_2 = 4HCl + S_2 + H_2S_2O_3$$

and

$$H_2S_2O_3 = S + H_2SO_3.$$

Sulphur monochloride acts powerfully on mercury. Sulphur is easily soluble in it; a cold saturated solution contains nearly 70 p.c. of sulphur.

Uses.—Sulphur chloride is used in defecating cane-juice and refining sugar, in the so-called Eastes' process.

Sulphur chloride is used in vulcanising indiarubber goods. The articles to be vulcanised are first coated with indiarubber in the usual way, and are then placed in a closed chamber in which sulphur chloride is vapourised, by which means the 'curing' or vulcanisation of the indiarubber is effected (Abbott, Patent, 1878, 166).

Parkes' process, which has been in use since 1846, consists in immersing the indiarubber goods in a solution of sulphur chloride in carbon disulphide for a few seconds. It is used extensively in preparing the surface of tobacco pouches, tubing, rings, &c.

Sulphur dichloride SCl_2 is prepared by passing dry chlorine into sulphur monochloride, when the liquid assumes a dark reddish-brown tint. The vessel containing the monochloride should be surrounded by a freezing mixture, and excess of chlorine removed by passing a current of carbon dioxide through the liquid (Hübner and Guerout, Z. 1870, 455). In combination the dichloride is more stable, forming definite compounds with arsenic trichloride, SCl_2AsCl_3 (Rose), and with ethylene, $C_2H_4SCl_2$, and amylene, $C_5H_{10}SCl_2$ (Guthrie). It is decomposed by water in the same way as sulphur monochloride, and on boiling is decomposed into the monochloride and chlorine.

Sulphur tetrachloride SCl_4. Michaelis has shown that this compound is formed when the dichloride of sulphur is saturated with chlorine at −22°. It is a mobile, transparent, light-brown liquid, and yields on analysis numbers agreeing with the formulæ SCl_4. Water decomposes it with violence, forming sulphurous and hydrochloric acids:

$$SCl_4 + 2OH_2 = SO_2 + 4HCl.$$

That sulphur tetrachloride is not merely a solution of chlorine in the dichloride is shown by the action of sulphur trioxide on it, thus:

$$SCl_4 + 2SO_3 = \underset{\text{Thionyl chloride.}}{SOCl_2} + \underset{\text{Pyrosulphuryl chloride.}}{S_2O_5Cl_2}.$$

SULPHURIC ACID. The substance formerly spoken of as 'sulphuric acid' or 'anhydrous sulphuric acid,' indicated by the formula SO_3, and consisting of 40 parts sulphur and 60 parts of oxygen in 100 parts, is now more systematically termed *sulphur trioxide* or *sulphuric anhydride*; when brought into contact with water energetic chemical action ensues, products being formed capable in all cases of representation by the formula mSO_3,nH_2O, and usually regarded as single homogeneous substances when m and n have certain simple integral values, but in other cases as mixtures of different substances, or as solutions of one or other of them in excess of water. The table on next page represents the leading 'sulphuric acids' or 'sulphuric hydrates' usually recognised as distinct compounds, either on account of their crystallinity or other well-marked physical peculiarity, or because of the existence of definite metallic salts derivable from them by replacement of the hydrogen by metals.

The existence of numerous hydrates, in addition to those above mentioned, has been inferred by S. U. Pickering from the study of various physical phenomena connected with acid of different strengths. One of these, $SO_3,5H_2O$ or $H_2SO_4,4H_2O$, has been isolated in hard well-defined crystals by cooling acid of approximately this strength. This hydrate melts at −25°C., whereas frozen acid containing either more or less water (within certain limits) melts at notably lower temperatures. On plotting a curve with the percentages of H_2SO_4 present as abscissæ, and the freezing points as ordinates, the curve descends from 0° (water only) to −75° at 38 p.c. of H_2SO_4, and then rises to a first maximum of −25° at 57·6 p.c., the new hydrate; after which it again falls to below −60°, rising again to a second maximum of +8·5° at 84·5 p.c., the hydrate $SO_3,2H_2O = H_2SO_4,H_2O$; then it falls again to near −40°, finally rising to a third maximum of +10·4° at 100 p.c.—*i.e.* the hydrate SO_3,H_2O. Addition of SO_3 to pure monohydrate, forming mSO_3,nH_2O, where $m > n$, causes the curve to sink again (C. J. Trans. 1890, 648, 331).

1. Physical properties of sulphuric acid. Commercially, sulphuric acids may be divided into two classes, viz. 'fuming acids' or substances indicated by the formula mSO_3,nH_2O, where $m > n$, the *ratio* $\frac{m}{n}$ varying from something not greatly exceeding 1 (fuming acids of low strength) up to a much higher number (practically

Formula	Name	Corresponding salt	Physical characters
SO_3	Sulphur trioxide . Sulphuric anhydride	None . . .	Crystalline solid.[1] M.p. 14·8°. B.p. 46·2° (Weber)
$4SO_3,H_2O = H_2S_4O_{13}$.	—	—	Liquid; depositing crystals at 8–10°
$2SO_3,H_2O = H_2S_2O_7$.	Pyrosulphuric acid 'Solid oleum'	Sodium pyrosulphate $Na_2S_2O_7$	Crystalline solid; m.p. 35°
$4SO_3,3H_2O = H_6S_4O_{15}$	-	—	Ditto; m.p. 26°
$SO_3,H_2O = H_2SO_4$.	Sulphuric acid . Monohydrated acid .	Acid salt $NaHSO_4$ Neutral salt Na_2SO_4	Liquid; begins to boil with decomposition at 290°; at low temperatures forms crystals; m.p. 10·5°
$SO_3,2H_2O = H_4SO_5$.	Dihydrated sulphuric acid (glacial acid)	Basic lead sulphate Pb_2SO_5	Crystallises at low temperatures; m.p. 8°
$SO_3,3H_2O = H_6SO_6$.	Trihydrated sulphuric acid; orthosulphuric acid	Mercuric orthosulphate (Turpeth mineral) Hg_3SO_6	Hydrate in formation of which the maximum amount of contraction takes place

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[1] An isomeric modification of higher melting and boiling points has been supposed to exist; but, according to Weber, this substance contains small quantities of combined water.

pure sulphuric anhydride), 'solid oleum' (approximately pyrosulphuric acid) being an intermediate variety where $\frac{m}{n}$ is not far from 2; and 'non-fuming acid' or 'vitriol' where $m < n$, varying from O.V. ('oil of vitriol'), where m very nearly $= n$, so that $\frac{m}{n}$ is but little less than 1, down to 'chamber acids' of sp.gr. 1·5 and less (100° Tw. and below). Acid of sp.gr. 1·65 (130° Tw.) is approximately orthosulphuric acid $SO_3,3H_2O$; and acid of sp.gr. 1·78 (156° Tw.) approximately dihydrated acid, $SO_3,2H_2O$. These and all weaker acids on heating lose water, becoming more and more concentrated until finally a product is obtained, boiling and distilling as a whole at somewhat above 300°, and containing between 98 and 99 p.c. of H_2SO_4 with a small balance of surplus water. Pure monohydrated acid cannot be obtained in this way, but is readily formed by adding to this (or to weaker acid or pure water) the appropriate amount of sulphuric anhydride; when obtained it cannot be distilled unchanged, the boiling-point rising from 290° to 338° (Marignac). The dihydrated acid readily separates in crystals from acid of strength near to 150-155° Tw. in cold weather, freezing of carboys containing such fluids being not infrequent in winter if kept in a cold situation. Crystalline monohydrated acid is similarly formed from oil of vitriol under favourable conditions; as a general rule, concentrated acid does not readily solidify in carboys, even in cold weather, unless a crystal of previously solidified acid is introduced; but the production of monohydrated acid by cooling O.V. of 96 to 98 p.c. to about −10°C., so that crystals form (the crystallisation being started by means of a portion of the crystals from a previous batch left in the vessel), and draining off the weaker unsolidified portion, has been shown by Marignac and Lunge to be readily practicable on a manufacturing scale, and acid thus further concentrated is now in the market (*v.* p. 759).

The following table of the freezing and melting and boiling points of acid below the strength of H_2SO_4 is compiled from the results obtained by Lunge (B. 1878, 370, and 1881, 2,649; Alkali Makers' Pocketbook, 94 and 95).

Per cent. H_2SO_4	Sp.gr.	Boiling-point	Freezing-point	Melting-point
5	1·031	101°	—	—
10	1·069	102	—	—
15	1·107	103·5	—	—
20	1·147	105	—	—
25	1·184	106·5	—	—
30	1·224	108	—	—
35	1·265	110	—	—
40	1·307	114	—	—
45	1·352	118·5	—	—
50	1·399	124	—	—
53	1·428	128·5	—	—
56	1·459	133	—	—
60	1·503	141·5	—	—
62·5	1·530	147	—	—
65	1·557	153·5	—	—
67·5	1·585	161	—	—
70	1·615	170	—	—
72	1·639	174·5		—
74	1·661	180·5	Liquid at −20°	—
76	1·688	189	Do.	—
78	1·710	199	Do.	—
79·5	1·727	—	−7·5	−7·5
80	1·733	207	−8·5	−8·5
81·3	1·749	—	−0·2	+4·5
82	1·758	218·5	—	
83·2	1·767	—	+1·6	+6·5
84	1·773	227	+8·5	+8·5
86	1·791	238·5	+4·5	+8·0
88	1·807	251·5	−9·0	−6·0
90	1·818	262·5	—	—
91	1·824	268	Liquid at −20	—
92	1·830	274·5	—	—
93	1·834	281·5	—	—
94	1·837	288·5	—	—
95	1·840	295	Liquid at −20	—

The specific gravity of dilute sulphuric acid of various degrees of concentration and at various temperatures has been examined by a number of chemists and physicists with results not always exhibiting as close concordance as might be desired; the earlier tables given by Vauquelin, d'Arcet, Ure, Parkes, &c., have long been regarded as superseded by the more exact ones of Bineau and Kolb.[1] For acids approaching the concentration of O.V. the sp.gr. is a fallacious test of strength, because acid of strength 98 p.c. H_2SO_4 has a maximum density as compared with either stronger or weaker acid; thus the following figures result from the experiments of Kohlrausch (P. 8, supplement p. 675) and of Lunge and Naef (S. C. I. 1883, 29, from Chem. Industrie, 5, 37, 1883).

Apart from this, the effect of temperature variation in altering the sp.gr. is greater, whilst the effect of a given increment in strength is less, the stronger the acid; so that in practice the sp.gr. is of little value in determining the strength of acid containing upwards of 90 p.c. H_2SO_4.

Per cent. H_2SO_4	Kohlrausch	Lunge and Naef
	Sp.gr. at 18° compared with water at 4°	Sp.gr. at 15°
90	1·8147	1·8185
91	1·8200	1·8241
92	1·8249	1·8294
93	1·8290	1·8339
94	1·8325	1·8372
95	1·8352	1·8390
96	1·8372	1·8406
97	1·8383	1·8410
98	1·8386	1·8412
99	1·8376	1·8403
100	1·8342	1·8384

The following table, recalculated by the author, represents the results obtained by Bineau (A. Ch. 3, 24, 341):

At 15°C.		Diminution in density for each 1° above 15°C.	Percentage SO_4H_2	Difference for 1°Tw.	Percentage SO_3	Difference for 1°Tw.
Degrees Tw.	Sp.gr.					
165	1·825	·188	90·60	—	73·96	—
160	1·800	·185	86·75	·77	70·81	·63
155	1·775	·183	83·83	·58	68·42	·48
150	1·750	·182	81·45	·48	66·49	·39
145	1·725	·181	79·25	·44	64·69	·36
140	1·700	·180	77·16	·42	62·98	·34
135	1·675	·179	75·00	·43	61·22	·35
130	1·650	·178	72·92	·42	59·52	·34
125	1·625	·176	70·83	·42	57·82	·34
120	1·600	·174	68·66	·43	56·06	·35
115	1·575	·172	66·58	·42	54·35	·34
110	1·550	·170	64·42	·43	52·59	·35
105	1·525	·167	62·18	·44	50·75	·37
100	1·500	·164	59·89	·46	48·89	·38
90	1·450	·160	55·19	·47	45·05	·39
80	1·400	·155	50·20	·50	40·98	·41
70	1·350	·148	44·89	·53	36·65	·43
60	1·300	·140	39·29	·56	32·07	·46
50	1·250	·131	33·29	·60	27·17	·49
40	1·200	·120	27·23	·61	22·23	·50
30	1·150	·100	20·79	·64	16·97	·52
20	1·100	·080	14·25	·65	11·63	·53
10	1·050	·047	7·50	·67	6·12	·55

The following tables are abridged from longer ones, founded on Kolb's experiments, which have been accepted as standard by the German Society of Alkali Makers (Lunge and Hurter, 'Alkali Makers' Pocket Book,' pp. 88–95).

At 60°F.=15·5°C.		100 parts by weight contain		1 litre contains kilos. of H_2SO_4	At 60°F.=15·5°C.		100 parts by weight contain		1 litre contains kilos. of H_2SO_4
Sp.gr.	Degrees Twaddell	SO_3	H_2SO_4		Sp.gr.	Degrees Twaddell	SO_3	H_2SO_4	
1·20	40	22·10	27·10	·325	1·30	60	32·02	39·23	·510
1·21	42	23·11	28·31	·342	1·31	62	33·00	40·42	·529
1·22	44	24·10	29·52	·360	1·32	64	33·97	41·61	·549
1·23	46	25·09	30·73	·378	1·33	66	34·89	42·73	·568
1·24	48	26·08	31·95	·396	1·34	68	35·25	43·79	·587
1·25	50	27·07	33·16	·414	1·35	70	36·62	44·85	·605
1·26	52	28·06	34·37	·433	1·36	72	37·48	45·91	·624
1·27	54	29·05	35·59	·451	1·37	74	38·35	46·97	·643
1·28	56	30·04	36·80	·470	1·38	76	39·20	48·02	·662
1·29	58	31·03	38·01	·490	1·39	78	40·05	49·06	·682

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[1] According to Lunge, the tables of Vauquelin and d'Arcet are still in use in the South of France (1891).

At 60°F.=15·5°C.		100 parts by weight contain		1 litre contains kilos. of H_2SO_4	At 60°F.=15·5°C.		100 parts by weight contain		1 litre contains kilos. of H_2SO_4
Sp.gr.	Degrees Twaddell	SO_3	H_2SO_4		Sp.gr.	Degrees Twaddell	SO_3	H_2SO_4	
1·40	80	40·90	50·10	·701	1·62	124	57·52	70·16	1·141
1·41	82	41·75	51·14	·721	1·63	126	58·22	71·32	1·162
1·42	84	42·60	52·18	·741	1·64	128	58·90	72·16	1·183
1·43	86	43·41	53·18	·761	1·65	130	59·60	73·00	1·204
1·44	88	44·20	54·15	·780	1·66	132	60·25	73·80	1·225
1·45	90	45·00	55·12	·799	1·67	134	60·90	74·60	1·247
1·46	92	45·79	56·09	·818	1·68	136	61·58	75·43	1·268
1·47	94	46·58	57·06	·838	1·69	138	62·28	76·29	1·289
1·48	96	47·34	58·00	·858	1·70	140	62·98	77·15	1·311
1·49	98	48·08	58·90	·877	1·71	142	63·68	78·01	1·333
1·50	100	48·81	59·80	·897	1·72	144	64·39	78·87	1·356
1·51	102	49·55	60·70	·917	1·73	146	65·09	79·73	1·379
1·52	104	50·28	61·60	·936	1·74	148	65·79	80·59	1·402
1·53	106	51·00	62·50	·956	1·75	150	66·49	81·45	1·425
1·54	108	52·73	63·40	·976	1·76	152	67·39	82·56	1·452
1·55	110	52·46	64·30	·996	1·77	154	68·30	83·67	1·480
1·56	112	53·20	65·20	1·017	1·78	156	69·20	84·78	1·509
1·57	114	53·94	66·10	1·037	1·79	158	70·11	85·89	1·537
1·58	116	54·68	66·98	1·058	1·80	160	71·02	87·00	1·566
1·59	118	55·39	67·85	1·078	1·805	161	71·58	87·69	1·582
1·60	120	56·10	68·72	1·099	1·81	162	72·15	88·39	1·599
1·61	122	56·81	69·59	1·120	1·815	163	72·71	89·88	1·616

Variation of specific gravity with temperature.

0°	10°	20°	30°	40°	50°	75°	100°
1·857	1·846	1·835	1·825	1·816	1·806	1·782	1·762
1·807	1·796	1·784	1·773	1·762	1·751	1·725	1·700
1·754	1·745	1·735	1·726	1·716	1·706	1·683	1·660
1·704	1·695	1·685	1·676	1·666	1·656	1·634	1·610
1·654	1·645	1·635	1·626	1·617	1·608	1·586	1·565
1·604	1·595	1·585	1·576	1·567	1·558	1·537	1·516
1·552	1·544	1·536	1·528	1·520	1·512	1·494	1·469
1·502	1·494	1·486	1·478	1·470	1·462	1·441	1·419
1·452	1·444	1·436	1·429	1·423	1·416	1·395	1·374
1·402	1·394	1·386	1·379	1·372	1·364		
1·352	1·344	1·336	1·330	1·324	1·316		
1·300	1·293	1·287	1·280	1·274	1·267		
1·250	1·243	1·237	1·230	1·224	1·217		
1·200	1·193	1·186	1·180	1·173	1·165		
1·149	1·143	1·137	1·131	1·125	1·119		
1·098	1·093	1·087	1·082	1·077	1·072		
1·048	1·043	1·037	1·032	1·028	1·022		

A number of careful observations have been made by Lunge and Isler (Zeit. f. angew. Chem. 1890, 129; also S. C. I. 1890, 500) leading to the deduction of a curve representing the variation of density with strength, the sp.gr. at $\frac{15°}{4°}$C. (absolute density at 15°C.) being the ordinate, and the strength the abscissa. In the main this curve agrees closely with the mean curve deduced from the experiments of Kolb, and of Bineau above quoted; but it differs measurably at the ends—*i.e.* in the case of the weakest and strongest acids.

S. U. Pickering has published (C. J. Trans. 1890, 64) a number of observations on the sp.gr. of sulphuric acid of strengths between 0·997007 and 99·85700 p.c. of H_2SO_4, in which it is claimed that the limit of error does not, as a rule, exceed 0·000008 (eight parts in one million), notwithstanding that the eight determinations of the strength of the strong sulphuric acid used to prepare other strengths by dilution varied between 99·704 and 99·962 p.c., showing a range of 0·258, or about 1 part in 400. Founded on these results, H. D. Richmond has calculated a table (S. C. I. 1890, 479) of specific gravities of sulphuric acid between the limits 1·8248 and 1·8384 referred to water at 15° (90·86 to 100 p.c.).

Another table, 'the result of a careful selection of figures from standard authorities,' has been calculated by A. H. Elliott (The Chemical Trade Journal, March 24, 1888, 182).

The specific gravity of commercial sulphuric acid, as compared with its strength, usually differs slightly from that found in the case of chemically pure acid, owing to the presence of sulphate of lead and other impurities.

Specific heat of dilute sulphuric acid. F. Bode gives the following table indicating the relationship between the sp.gr. at 15°C., and the specific heat of sulphuric acid (Zeit. f. angew. Chem. 1889, 244; also S. C. I. 1889, 543).

Specific gravity	Degrees Baumé	Specific heat	Specific gravity	Degrees Baumé	Specific heat
1·842	66	0·3315	1·320	35	0·67
1·774	63	0·38	1·263	30	0·73
1·711	60	0·41	1·210	25	0·78
1·615	55	0·45	1·162	20	0·82
1·530	50	0·49	1·116	15	0·87
1·453	45	0·55	1·075	10	0·90
1·383	40	0·60	1·037	5	0·95

A number of determinations of the heat capacity of sulphuric acid solutions of different strengths have also been recorded by S. U. Pickering (C. J. Tr. 1890, 64).

Tension of aqueous vapour emitted by dilute sulphuric acid. E. Sorel has made a number of experiments, leading to the following results, abridged from much fuller tables (Bull. Soc. Ind. Mulhouse, 1890, 240; also S. C. I. 1890, 175). The figures represent tensions in millimetres of mercury; obviously they are much below the tensions of aqueous vapour in contact with water.

Percentage of H_2SO_4 in acid	Temperature								
	10°	20°	30°	40°	50°	60°	70°	80°	90°
44	4·4	8·5	15·5	28·1	48·3	—	—	—	—
48	3·7	7·1	13·4	23·9	40·1	69·0	107·2	—	—
52	3·0	5·8	10·9	18·9	31·5	54·0	84·5	131·2	207·9
56	2·2	4·3	8·1	14·2	24·1	41·6	65·0	100·9	160·0
60	1·6	3·0	6·1	10·0	16·9	28·7	46·1	72·3	118·7
64	1·2	2·2	4·0	6·5	10·9	18·7	30·3	48·0	83·7
68	·9	1·5	3·0	4·5	7·2	12·3	19·4	31·4	56·0
72	·7	1·0	2·0	3·2	4·8	7·5	12·0	20·0	33·7
76	·4	·5	1·4	2·1	3·0	4·8	7·5	11·8	18·5
80	·2	·3	·8	1·3	1·9	2·9	4·1	6·2	9·3

Tension of nitrous anhydride dissolved in sulphuric acid at different temperatures. E. Sorel (*l.c. supra*) has made a number of determinations of the amounts of nitrous anhydride given off when sulphuric acid of different strengths, and containing different proportions of dissolved nitrous gases, was made to flow through a spiral tube 5 metres long placed in a water-bath at constant temperature, whilst a current of pure nitrogen gas passed through the spiral in the opposite direction; the results obtained varied from ·009 milligram of N_2O_3 per litre of nitrogen at 0°, and 760 mm., when acid of sp.gr. 1·774, containing 28·4 grms. N_2O_3 per litre, was passed through at 40·1°C., up to 109·15 milligrams, when acid of sp.gr. 1·597, containing 12·5 grms. N_2O_3 per litre, was passed through at 89·9°C.; in general, the weaker the acid and the higher the temperature the more N_2O_3 was evolved.

G. Lunge (Zeit. f. angew. Chem. 1891, 37; also S. C. I. 1891, 364) has carried out a large number of further observations on this point, employing substantially the same method, with the difference that carbon dioxide was used instead of nitrogen, and a 10-bulbed tube instead of a spiral. Pure nitrosulphonic acid dissolved in pure sulphuric acid was used; no nitric acid was found in the solution. The following tables, representing grms. per litre throughout, are abridged from those given for nitrous vitriol of gravity respectively 1·720, 1·686, 1·633, and 1·60, and for temperatures of 50°–90°C. When plotted as curves, the figures show that in presence of strong acid, and at low temperatures, nitrosulphonic acid exists as a compound in the fluid; but, on diluting the liquid and raising the temperature, the compound is dissociated, and the nitrous acid formed removed by the gases into which it diffuses.

Loss of N_2O_3 *after* 1 *hour, during which time* 5 *litres of* CO_2 *were passed.*

Originally present	50°	60°	70°	80°	90°
Nitrous vitriol, sp.gr. 1·72 = 78 *p.c.* H_2SO_4.					
1	—	—	—	—	·006
5	—	—	—	—	·037
10	—	—	—	·018	·093
15	—	—	·006	·056	·193
20	—	—	·031	·150	·356
25	·012	·031	·125	·312	·600
30	·081	·125	·293	·550	·956
35	·156	·312	·525	·868	1·375
40	·268	·500	·775	1·193	1·800
45	·406	·712	1·050	1·537	2·337
50	·550	·931	1·325	1·875	2·675
Nitrous vitriol, sp.gr. 1·686 = 76 *p.c.* H_2SO_4.					
8	—	—	—	—	·025
10	—	—	—	·012	·050
15	—	—	·025	·100	·225
20	—	·050	·186	·425	·625
25	·010	·200	·462	1·025	1·662
30	·062	·362	·750	1·700	2·812
35	·275	·625	1·250	2·362	4·175
40	·486	·886	1·736	3·025	5·550
45	·825	1·300	2·325	3·736	6·975
49	1·100	1·650	2·886	4·236	8·100
Nitrous vitriol, sp.gr. 1·633 = 71½ *p.c.* H_2SO_4.					
1	·012	·025	·036	·100	·150
5	·212	·300	·436	·736	·825
10	·700	·936	1·436	2·086	2·375
15	1·186	1·675	2·412	3·450	4·162
20	1·662	2·412	3·400	4·850	5·986
25	2·700	3·636	5·000	6·800	8·662
30	4·412	5·412	7·350	9·675	13·125
32	5·236	6·325	8·575	11·175	16·362

Loss of N_2O_3 *after* 1 *hour, &c.*—continued.

Originally present	50°	60°	70°	80°	90°
Nitrous vitriol, sp.gr. 1·60 = 69 *p.c.* H_2SO_4.					
1	·050	·086	·175	·336	·412
5	·812	1·150	1·500	2·120	2·700
10	1·975	2·812	3·712	4·990	6·475
15	3·360	4·612	6·125	8·100	10·625
20	4·700	6·425	8·562	11·850	14·800

Fuming acid is generally valued in proportion to the amount of trioxide present, the balance being H_2SO_4. The sp.gr. is sometimes employed as a test of strength, but is fallacious, since the density of acid containing about 70 p.c. of SO_3 is a maximum, both stronger and weaker acids exhibiting lower densities. The following table is given by R. Messel (S. C. I. 1885, 573), all the specimens being liquid at 26·6°C.

Physical character at 60° F.	Percentage of SO_3	Specific gravity	
		At 80° F. = 26·6° C.	Calculated to 60° F. = 15·5° C.
—	8·3	1·842	1·852
Liquid . .	30·0	1·930	1·940
Crystalline mass resembling nitre	40·0	1·956	1·970
	44·5	1·961	1·975
	46·2	1·963	1·977
—	59·4	1·980	1·994
Liquid . .	60·8	1·992	2·006
	65·0	1·992	2·006
	69·4	2·002	2·016
Crystalline .	72·8	1·984	1·998
	80·0	1·959	1·973
	82·0	1·953	1·967

C. Winkler has obtained values slightly differing from Messel's, the acid used being 'commercial,' and therefore possibly not quite pure.

Specific gravity at 20°C.	Percentage of SO_3
1·860	1·54
1·870	4·28
1·880	6·42
1·890	8·16
1·900	10·07
1·910	11·43
1·920	15·95
1·930	21·34
1·940	28·03
1·950	31·46
1·960	35·87
1·970	44·64

A more accurate method consists in weighing out a portion of the acid to be examined in a sealed bulb,[1] which is then broken under water by shaking up in a bottle; sulphurous acid, generally present, is first determined by titration with iodine solution, and then the SO_3 by precipitation as barium sulphate or volumetrically (Messel, *l.c.*, p. 521). The following table is abridged from a longer one given by Lunge and Hurter ('Alkali Makers' Pocket Book,' p. 96), for the reduction of percentages of total SO_3 thus found to percentages of SO_3, the balance being H_2SO_4.

Total SO_3 found by analysis	Contains per cent.	
	SO_4H_2	SO_3
81·63	100	0
82·00	98	2
82·37	96	4
82·73	94	6
83·10	92	8
83·47	90	10
83·84	88	12
84·20	86	14
84·57	84	16
84·94	82	18
85·31	80	20
85·67	78	22
86·04	76	24
86·41	74	26
86·78	72	28
87·14	70	30
87·51	68	32
87·88	66	34
88·24	64	36
88·61	62	38
88·98	60	40
89·35	58	42
89·71	56	44
90·08	54	46
90·45	52	48
90·82	50	50
91·18	48	52
91·55	46	54
91·92	44	56
92·29	42	58
92·65	40	60
93·02	38	62
93·39	36	64
93·76	34	66
94·12	32	68
94·49	30	70
94·86	28	72
95·22	26	74
95·59	24	76
95·96	22	78
96·33	20	80
96·69	18	82
97·06	16	84
97·43	14	86
97·80	12	88
98·16	10	90
98·53	8	92
98·90	6	94
99·27	4	96
99·63	2	98
100·00	0	100

Setlik finds (Chem. Zeit. 13, 1,670; C. J. Abs. 1890, 414; S. C. I. 1890, 417) that a simple method of valuation, with sufficient accuracy for most purposes, is to titrate 100 grms. in a flask with water until the acid ceases to give off fumes, the flask being kept cool. At first a thick cloud is formed on the addition of each drop, but latterly the fumes become less apparent. The flask must then be shaken after each addition of water until the fumes are absorbed before adding the next portion: 1 c.c. of water represents 4·444 grms. SO_3. Acids containing more than 35 p.c. of SO_3 should be diluted down to about that strength by addition of pure H_2SO_4. Lunge regards this method as insufficiently accurate for use between buyer and seller, although otherwise convenient.

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[1] Instead of a sealed bulb, a special form of 'bulb-tap pipette' is recommended by Lunge and Rey (Zeit. f. angew. Chem. 1891, 165).

Dilute free sulphuric occurs in nature in considerable quantities in various streams and lakes, *e.g.* the Rio Vinagre in South America, and Lake Mount Indien in Java; probably in such cases it is formed by the spontaneous oxidation of natural sulphides, or by the action of water containing chlorides on certain silicates and sulphates conjointly, under the influence of internal terrestrial heat. The drainage waters of copper mines and others where pyrites becomes exposed to the air often contain sufficient quantities to exert a highly corrosive influence on the pumps and machinery. As an artificial product it has been known for centuries, obtained by distilling various sulphates, especially alum and copperas (ferrous sulphate), either alone or with silicious matter; in this way a highly corrosive powerfully acid distillate is obtained, consisting, under favourable circumstances, of monohydrated sulphuric acid containing sufficient sulphuric anhydride dissolved therein to fume slightly; from the oily consistency of the product the common name 'oil of vitriol' is derived. It has also long been known that when brimstone and a small quantity of saltpetre are burnt together in moist air, or in vessels containing water to absorb the fumes produced, an acid liquid results which can be concentrated by evaporation. The chemical identity of the two products, however, does not seem to have been clearly understood until the beginning of the seventeenth century, and not till near 1740 was the manufacture of sulphuric acid by processes of the latter kind carried out on anything like a moderately large scale. About this time, however, Ward set up at Richmond, in Surrey, a small factory for the preparation of sulphuric acid 'per campanam' (made by the bell), so called from the shape of the glass vessel in which the sulphur and saltpetre were burnt together (about 8 parts of the former to 1 of the latter), the lower part containing water kept warm by a sand-bath. Repeated charges were fired inside the bell at intervals, so that the fumes produced by one charge should be condensed as far as possible before the next one was fired; ultimately the watery acid obtained became strong enough for use, either at once or after concentration by evaporation in glass retorts, and the process became so far a commercial success that the acid thus produced could be profitably sold at only a small fraction of the price previously charged for acid prepared by distilling green vitriol. Since that time the manufacture of non-fuming sulphuric acid from sulphur has developed into one of the largest chemical industries extant; but until recently the production of fuming acid has remained comparatively but small. Certain developments of the coal-tar colour industry, however, have of late created a considerable demand for fuming acid, in consequence of which processes of manufacture have been adopted based on principles entirely different from that involved in the production of 'Nordhausen' acid by distillation of sulphates—namely, the direct union of sulphur dioxide and oxygen to form sulphur trioxide, either in the entire absence of water, or in presence of a quantity insufficient to hydrate the product to such an extent as to prevent fuming. This direct union will not readily take place unless some solid body be present, the surface action of which promotes the combination of the two gases; platinum, especially when in fine division, possesses this power to a remarkable extent, but numerous other substances, such as various metallic oxides and even brickwork, are more or less active in this direction. The formation of vitriol from the combustion of sulphur depends likewise on the indirect addition of oxygen to sulphur dioxide, but in this case the surface action of solid substances is not requisite, oxides of nitrogen being used instead to effect the combustion; moreover, the action here takes place in presence of an excess of aqueous vapour, so that the resulting acid is usually weaker than orthosulphuric acid, and requires concentration by evaporation if oil of vitriol is to be manufactured. Accordingly, the plant used in the production of vitriol is for the most part entirely different from that employed to manufacture fuming acid, saving in so far as vitriol made from sulphur is employed as raw material for the production of the latter.

2. **Manufacture of fuming acid.** A considerable number of processes for the production of fuming acid have been at various times patented, and more or less put in actual operation; these may conveniently be grouped in three divisions—namely (1) those depending on the action of heat on some metallic sulphate, whereby decomposition is brought about with evolution of sulphur trioxide, more or less decomposed further into sulphur dioxide and oxygen by the temperature employed; (2) those in which the essential action is the surface operation of certain solids in bringing about union between sulphur dioxide and oxygen; and (3) those based on other reactions. Obviously the first two principles might be combined together, the surface action being employed to reproduce sulphur trioxide from the mixture of dioxide and oxygen resulting from the partial breaking up of trioxide by heat in distilling sulphates; this class of combination process was patented by Neale (1876), and is stated to be in actual use; but inasmuch as the most effective methods employed in fuming acid works are carefully kept secret, little or no reliable published information on the subject is extant.

(1) *Processes of distillation of sulphates.* Probably the substance most largely employed, at any rate until recently, as a source of fuming acid is *sulphate of iron*, formerly in the form of 'copperas' or 'green vitriol' (ferrous sulphate), carefully dried so as to deprive it of most of its water of crystallisation and partially peroxidise it during the process; latterly in the form of crude ferric sulphate prepared by long-continued weathering of certain slaty minerals containing iron sulphide disseminated throughout them, lixiviation of the mass, evaporation of the mixed ferrous, ferric, and aluminic sulphates dissolved out, and gently roasting, so as to dehydrate the mass and completely peroxi-

dise the iron present. On heating such materials in a series of clay retorts mounted together in a large 'galley' furnace, sulphur trioxide is expelled when the temperature rises sufficiently high, and is condensed in receivers previously charged either with a small quantity of water or preferably with oil of vitriol or weak fuming acid from a previous operation. Several successive charges are worked off into the same set of receivers, each retort holding only a comparatively small quantity, not exceeding 3 kilos of 'vitriol-stone'; the residuum of impure ferric oxide, more or less brightly tinted, left in the retort is so far from being valueless that it practically constitutes as important a product as the fuming acid itself, especially in the case of certain shades in the production of which so high a temperature is requisite that a very large portion of the anhydride is lost by splitting up into sulphur dioxide and oxygen; by the use of various subsidiary processes the residue is converted into pigments of different shades and considerable value. By submitting to redistillation, at a gentle heat, the fuming acid thus prepared, almost pure sulphur trioxide can be obtained; or by receiving the vapours in fuming acid of lower strength, fuming acid of any required higher strength may be produced; thus fuming acid containing 98 p.c. of trioxide and 2 p.c. of H_2SO_4 is now obtainable commercially by the ton, whereas a few years ago it was a mere chemical curiosity of which comparatively few persons had ever seen so large a quantity as one pound at once.

R. Schubert has patented a process for effecting the distillation under greatly diminished pressure, the vapours evolved being passed through heated platinised asbestos, so as to cause the reunion of the sulphur dioxide and oxygen formed by the breaking up of sulphur trioxide under the influence of heat.

Instead of ferric sulphate, *magnesium sulphate* has been proposed for use (Sonstadt, 1875); the high temperature required to decompose the salt causes much loss by conversion into sulphur dioxide and oxygen. *Sodium pyrosulphate*, obtained by carefully heating sodium hydrogen sulphate, was proposed by Prelier in 1847, and re-patented by Wallace in 1876; the reactions here are

$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$$
$$2NaHSO_4 = H_2O + Na_2S_2O_7$$
$$Na_2S_2O_7 = Na_2SO_4 + SO_3,$$

so that the process is a continuous one, the neutral sodium sulphate resulting from the distillation being converted into sodium hydrogen sulphate by treatment with sulphuric acid, and so on, over and over again. Wolters has patented the analogous use of mixed magnesium sulphate and sodium or potassium pyrosulphate, which is stated to give off sulphur trioxide at a lower temperature than the pyrosulphate alone, and so to diminish the loss by formation of sulphur dioxide; unless a high temperature be employed the magnesium sulphate does not suffer decomposition, but even if it should be decomposed, obviously the resulting magnesium oxide will reproduce sulphate on treating with sulphuric acid. Processes based on the action of heat on pyrosulphates do not appear to have met with much commercial success; but a method due to Wolters is said by Lunge to be actually at work in several factories: this consists in treating sodium pyrosulphate with monohydrated sulphuric acid, when sulphur trioxide is formed together with sodium hydrogen sulphate, thus: $Na_2S_2O_7 + H_2SO_4 = 2NaHSO_4 + SO_3$. By heating the residual acid sodium sulphate to 300°–320° in a retort furnished with an agitator and connected with an air-pump, it is easily and completely converted into pyrosulphate, with loss of water. Winkler has applied the continuous principle to the reproduction of ferric sulphate in the iron process, starting from burnt pyrites or other form of ferric oxide, so as to render the working continuous and independent of the supply of copperas or 'vitriol stone,' practically only obtainable in certain special localities. After the distillation is completed, the 'caput mortuum' is treated with sulphuric acid so as to reproduce ferric sulphate. Scheurer-Kestner finds that by heating to a bright-red heat a mixture of 2 parts of calcium sulphate (gypsum) and one of ferric oxide, much sulphuric anhydride is evolved as such, comparatively little being broken up into sulphur dioxide and oxygen until the latter part of the heating; addition of a little calcium chloride or fluoride to the mixture considerably retards the breaking up. Sulphates of other dibasic metals, *e.g.* lead and magnesium—may be substituted for calcium sulphate. Cummings (Eng. Pat. 7,355, 1886) heats gypsum intimately mixed with clay and moulded into bricks in a kiln, whereby silicate of lime and alumina is formed suitable for hydraulic cement, whilst sulphuric anhydride is evolved, more or less decomposed by the heat into sulphur dioxide and oxygen. S. Pitt has patented a process whereby sulphuric anhydride is obtained from the acid residues of petroleum refining, &c., consisting of conversion into ferric sulphate by addition of red ochre, and heating in a current of air to 300°–350°C. Ferrous sulphate is formed and remains, whilst one-third of the sulphur present is expelled as sulphuric anhydride, which is condensed (S. C. I. 1888, 628). J. D. Stark has patented a somewhat similar process, whereby the residues are fed into a retort by means of an endless screw; the heat causes sulphur dioxide to be evolved, which is cooled and washed, mixed with air or oxygen in the proper proportion, and passed through tubes containing contact agents—*e.g.* platinised asbestos (S. C. I. 1890, 734).

(2) S[illegible]. It has long been known as a laboratory experiment that when a mixture of sulphur dioxide and oxygen is passed through a tube containing heated platinum, combination is induced and sulphur trioxide formed; more than fifty years ago attempts were made to utilise the reaction in vitriol-making, and so to dispense with the use of nitre; thus Phillips in 1831 patented a process of this kind, brimstone being burnt in excess of air, so that the gaseous mixture contained sufficient oxygen, and the gases, mixed with aqueous vapour, being brought into contact with hot platinum. In practice, however, the process proved unable to compete with the ordinary nitre process as regards cheapness of product; and the same result followed in several subsequent cases where attempts to manufacture

vitriol by 'catalytic' action were made, the principle involved being the same throughout, but with more or less difference in details. In 1875 Winkler pointed out that the reaction might be used as a source of sulphuric anhydride and fuming acid, so as to compete commercially with the distillation process; platinised asbestos (prepared by dipping asbestos successively in platinic chloride and sal-ammoniac solutions, drying, and igniting) being highly effective in bringing about the required surface action, and a largely increased yield being obtained when the sulphur dioxide and oxygen are not diluted with nitrogen—*e.g.* when prepared by decomposing ordinary oil of vitriol by heat into sulphur dioxide, oxygen, and steam, and removing the last by condensation, precisely as in Deville and Debray's process for the manufacture of oxygen from vitriol, saving that the sulphur dioxide is not required to be removed as well as the aqueous vapour. In the same year, Squire and Messel patented in Britain a process based on much the same lines, employing platinised pumice stone as the 'catalytic' agent. The principal difficulty in applying this process industrially was the rapid corrosive action exerted upon that part of the plant where the sulphuric acid was decomposed by heat. Fig. 1 represents an arrangement for the purpose, patented by Angerstein (Germ. Pat. 26,959, 1883), the acid being supplied by an inverted siphon *b b* to a platinum cup *c*, supported by a perforated porcelain nozzle *p*, placed at the base of a tubular furnace of firebricks heated by producer gas and air (both previously heated, and under pressure) supplied from their respective mains *l* and *g*, through orifices at regular intervals *k k*, *m m*, and *n n*, so as to heat up the tubular interior *f f* intensely; concentrically within the tube are a series of socket pipes *d d d* of fireclay, one above the other, each provided with a perforated bottom on which lumps of clay are piled. The sulphuric acid is volatilised in the platinum basin *c*, and the vapours passing upwards are decomposed by the incandescent clay. Other forms of apparatus for the same purpose have been patented by Squire.

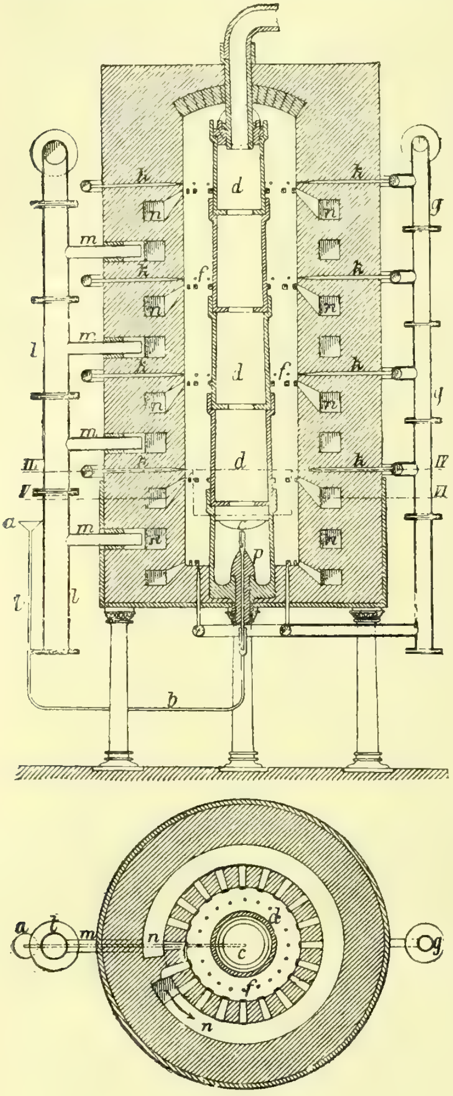

FIG. 1.

Numerous improvements have from time to time been made the subjects of patents; thus in 1878 Winkler (Germ. Pat. 4,566, Sept. 21) patented the use of a variety of 'catalytic' agents of high activity, more especially such substances as asbestos, slag wool, infusorial earth, &c., or even organic bodies like cellulose or cotton-wool, impregnated with platinum black by soaking in platinum chloride solution and reducing with sodium formate; surface-acting materials of this kind are stated to be sufficiently active to enable sulphuric anhydride to be readily made from burner gases containing as little as 4 p.c. of sulphur dioxide.[1] Messel (1878) patented the employment of sulphur dioxide and oxygen made by burning sulphur in excess of electrolytic oxygen prepared by a dynamo machine;[2] and Neale (1876) the employment of the mixture of sulphur dioxide and oxygen given off (along with more or less sulphur trioxide) by heating various sulphates, platinised asbestos, spongy platinum, or oxide of copper, iron, or chromium, &c., being used as surface-acting material. In 1882 Rath took out a patent for the use of ordinary burner gases (sulphur or pyrites burnt in air) passed through purifiers for removing dust and aqueous vapour, and then through vertical iron tubes containing surface-acting materials at a temperature between a low and a full red heat. A patent (9,188, 1887) has been taken out by Hänisch and Schröder claiming the application of increased pressure to facilitate the contact action, a mixture of 25 p.c. pure sulphur dioxide and 75 p.c. air being the most effective proportion. According to Lunge, this process is carried out in several large factories, and is probably the most successful of those now working (1891). It is obvious that when the manufacture of ordinary sulphuric acid is conjoined with that of fuming acid the loss that would otherwise be occasioned through imperfect peroxidation of sulphur dioxide may be avoided by leading the exit gases into the vitriol chamber; so that under these circumstances the smaller relative yield obtained when gases diluted with nitrogen are employed is not necessarily fatal to the commercial success of the process; and in point of fact it is commonly understood that methods based on the combustion of sulphur or sulphides in air and formation of fuming acid by bringing the products of combustion into contact with energetic surface-acting materials are those principally employed in the manufacture of fuming acid.

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[1] Platinum black reduced by formaldehyde is the most active variety of all (Loew, B. 1890, 289).

[2] A somewhat similar patent, involving the use of pure oxygen instead of air, has been subsequently taken out by Lunge, sulphur or pyrites being burnt in excess of oxygen (prepared by Brin's process from air), and the resulting gases passed over contact agents.

(3) *Miscellaneous processes.*—Reactions other than the foregoing are capable of giving rise to fuming acid, and have accordingly been patented, but as yet do not appear to have come extensively into actual use. Amongst them may be noticed Grüber's nitrosulphonic acid process (1883), depending on the formation of nitrosulphonic acid (chamber crystals), $SO_2(OH)(NO_2)$, by the well-known reaction of ordinary burner gases and oxides of nitrogen on one another in presence of an amount of steam insufficient to form vitriol, and the action on these in a separate vessel of hot sulphur dioxide mixed with oxygen or air, whereby oxides of nitrogen are eliminated, which are led away to the ordinary vitriol chamber and there utilised, whilst a fuming acid is formed, probably chiefly in accordance with the equation—

$$2SO_2(OH)(NO_2) + SO_2 = 2NO + H_2SO_4 + 2SO_3.$$

Nobel and Fehrenbach have patented (1884) a process based on the direct dehydration of oil of vitriol by metaphosphoric acid, or even more highly hydrated phosphoric acid (glacial acid); at a temperature of about 320° this material converts the sulphuric acid into anhydride, retaining the water, which can be driven off at a higher temperature so as to reproduce the glacial phosphoric acid ready for use over again. By operating in a vessel filled at intervals with lumps of glacial phosphoric acid through a manhole, and provided with an exit tube at the bottom for the fluid solution of phosphoric acid formed, the process can be worked tolerably continuously. According to Lunge, no material is known that will withstand for a sufficient length of time the action of fused phosphoric acid, neither glass nor platinum being available.

3. **Manufacture of non-fuming acid.** Since Ward's time, during the last century and a half, the changes that have taken place in the nature of the plant used in preparing vitriol have rather been characterised by increase in dimensions than by anything involving a material variation in the general character of the process. About 1746 Roebuck substituted lead vessels or 'chambers' for glass bells; some fifty or sixty years later the use of steam, generated in a separate boiler, and of a more or less continuous current of air (instead of an intermittent supply obtained by opening valves in the chamber before igniting a fresh charge), with a sulphur burner separate from the leaden chamber, were introduced; since which time the leading alterations and improvements that have been made in the manufacture have been, firstly, the substitution for brimstone of pyrites and other metallic sulphides; and secondly, the addition of Gay-Lussac and Glover towers for the purpose of recovering nitrous fumes carried away in the spent gases or contained in the chamber acid, and of economising fuel by utilising the heat evolved in the combustion of the sulphur itself for concentrating by evaporation the somewhat dilute acid obtained in the chambers, and for supplying aqueous vapour to the gases, so as to diminish the amount of steam requisite to be generated by the combustion of ordinary fuel. Minor variations in the mode of supplying nitrous fumes have also been made, and the use of water spray instead of steam has been introduced by Sprengel and others, although this latter process has not been very widely adopted; with these exceptions, however, the vitriol manufacture has undergone little radical alteration during the last three quarters of a century, saving that the appliances now used are gigantic in dimensions compared with those employed at the commencement of that period, and that the processes are now carried out with far more precision under skilled and scientific supervision, with the result of obtaining a far larger yield from a given quantity of raw material at greatly decreased cost for labour, &c.

The substitution of pyrites for brimstone can hardly be classed as an improvement from the point of view of obtaining a purer product and of simplifying the appliances requisite, because, firstly, iron, arsenic, and other impurities are apt to be introduced into pyrites acid to a much greater extent than with brimstone; and secondly, more chamber space is rendered imperative for a given quantity of vitriol made, on account of the larger dilution of the sulphur dioxide produced from pyrites in virtue of the absorption of oxygen by the iron therein present, whereby a relatively much larger proportion of nitrogen becomes mixed with the products of combustion. These disadvantages, however, are for most purposes much more than counterbalanced by the greater cheapness of combined sulphur in the form of metallic ore, especially pyrites, than in that of brimstone. For some of the largest applications of vitriol (*e.g.* the manufacture by the Leblanc process of saltcake, or crude sodium sulphate, for glass-making and alkali-making; the preparation of superphosphate, ammonium sulphate, and artificial manures generally; and a variety of allied industries) the impurities derived from pyrites are of little or no consequence; but for certain other purposes these impurities are so far injurious that it is essential to employ a purer acid made from brimstone, even though this be more costly to prepare. Accordingly, even at the present day there is still a not inconsiderable production of brimstone acid in Great Britain to meet these special requirements; whilst abroad, and more especially in the United States (where for a variety of reasons the disproportion between the price of brimstone and pyrites suitable for vitriol-making is in many localities not so great as elsewhere), the manufacture of brimstone acid is carried out to a still larger extent as compared with that of pyrites acid.[1] If at any future time the price of brimstone should fall to such an extent as to render it possible to use that substance economically, the employment of pyrites would doubtless largely or entirely cease; the profitable use of certain kinds of this mineral has indeed been rendered practically impossible, excepting in certain districts, during the last twenty or thirty years on account of the advantages obtained by the employment of certain other kinds containing small quantities of copper, the extraction of which from the cinders left when the sulphur in the mineral is largely burnt off (by a method distinct from smelting, and generally known as the 'wet' process—*v.* COPPER) is now generally combined with, or made a supplement to, the manufacture of vitriol in the first instance. Whereas formerly ores, such as Wicklow pyrites, containing only about 30 p.c. of actual sulphur and a large admixture of slaty gangue, were largely exported and consumed as sources of vitriol; at the present day these ores can hardly compete in the market, especially when freight over long distances is considered, with 'cupreous ores' such as those obtained largely from Spain and Portugal, containing some 48 p.c. of sulphur, and only a few p.c.'s of siliceous gangue, which does not interfere with the subsequent process for copper extraction in the way that larger amounts of gangue would do, especially if of argillaceous character. Moreover, even if the poorer non-cupriferous ore could be profitably mined and carried long distances at the same price for a given amount of sulphur present as the richer cupreous ores, the latter would still be practically cheaper to use for a variety of reasons which will be discussed presently (*v.* p. 720).

Composition of brimstone and pyrites.—Commercial brimstone is usually tolerably pure sulphur containing little or nothing which will contaminate injuriously vitriol made therefrom, but leaving behind a small quantity of ash on incineration, varying in amount from a few tenths up to 2 or 3 p.c., or even more; its quality and consequent price is usually regulated rather by the colour and size of fragments, freedom from dust and smalls, and such like considerations, than by the nature of the small quantity of impurities present as determined by chemical analysis. Pyrites, on the other hand, is usually of a value dependent quite as much on the quantity of copper present as on the precise amount of sulphur contained. Pure iron disulphide, FeS_2, contains 46·7 p.c. of iron and 53·3 of sulphur; and pure copper pyrites (*chalcopyrite*), $FeCuS_2$ or Cu_2S,Fe_2S_3, contains iron = 30·6, sulphur = 34·9, and copper = 34·5 p.c. The cupreous ores principally used as sources of sulphur for vitriol-making are usually mixtures of these two substances, together with more or less gangue and small quantities of other metallic sulphides, especially those of arsenic, zinc, and lead, the copper pyrites being present to such an extent as to cause the whole mass to contain a few per cents. of metallic copper, but iron disulphide constituting the great bulk thereof. The analyses on next page will furnish an idea of the general character of various kinds of pyrites that either are, or have been, somewhat extensively used for the manufacture of sulphuric acid; those marked 'average' being the mean composition of quantities of many thousands of tons used during upwards of a twelvemonth, as determined by analyses made by the author, whilst the others are mostly derived from smaller quantities.

It is noticeable that several of these ores contain copper in very appreciable amounts, but are practically of no greater value for that reason, because the nature and amount of the gangue present prevents the ordinary 'wet' process of copper extraction being profitably applied to the cinders. A certain amount of the copper may sometimes be extracted very simply by weathering the burnt ore—*i.e.* exposing it freely to the atmosphere—whereby more or less copper sulphate is formed (together with other soluble salts) by spontaneous oxidation of the copper sulphide contained in the kernels; the liquor that drains from the heap (moistened by watering if requisite) being received in a tank filled with scrap iron, the copper is precipitated from the solution with very little labour. This process is actually used in some French works burning Chessy ore (Lunge, Sulphuric Acid, 1891, 2nd edition, p. 41).

The valuation of brimstone and pyrites, as regards the amount of sulphur present therein, is best effected by the following methods, accepted by the German Society of Alkali Makers (Hurter and Lunge, Alkali Makers' Pocket-book). 50 grams of finely-ground brimstone are dissolved in 200 c.c. of carbon disulphide in a well-stoppered bottle, and the sp.gr. of the solution, s, determined at a convenient temperature $t°$; the sp.gr. at 15°, S, is then calculated by the formula (valid up to 25°C.) $S = s \times ·00014(t - 15)$, and the percentage of sulphur deduced from the following table (abridged):—

S	Percentage of sulphur	S	Percentage of sulphur
1·271	4×0	1·321	$4 \times 12·1$
1·274	$4 \times 0·6$	1·324	$4 \times 12·8$
1·276	$4 \times 1·2$	1·327	$4 \times 13·5$
1·279	$4 \times 1·9$	1·330	$4 \times 14·2$
1·282	$4 \times 2·6$	1·333	$4 \times 15·0$
1·285	$4 \times 3·4$	1·336	$4 \times 15·6$
1·288	$4 \times 4·1$	1·339	$4 \times 16·4$
1·291	$4 \times 4·8$	1·342	$4 \times 17·1$
1·294	$4 \times 5·6$	1·345	$4 \times 17·9$
1·297	$4 \times 6·3$	1·348	$4 \times 18·6$
1·300	$4 \times 7·0$	1·351	$4 \times 19·3$
1·303	$4 \times 7·8$	1·354	$4 \times 20·1$
1·306	$4 \times 8·5$	1·357	$4 \times 21·0$
1·309	$4 \times 9·2$	1·360	$4 \times 21·8$
1·312	$4 \times 9·9$	1·363	$4 \times 22·7$
1·315	$4 \times 10·6$	1·366	$4 \times 23·6$
1·318	$4 \times 11·3$	1·369	$4 \times 24·8$

[1] Out of a total make estimated at 395,000 tons of oil of vitriol in America in 1885, W. Martyn calculated that the proportion made from pyrites (American, Canadian, and imported jointly) would be equal to a consumption of 75,000 tons pyrites, representing probably some 105,000 tons of oil of vitriol; or between $\frac{2}{3}$ and $\frac{3}{4}$ of the total make was estimated to be brimstone acid (W. Martyn, S. C. I. 1885, p. 26). In 1886 the quantity of pyrites imported had risen to 57,000 tons, that consumed for acid-making where mined being 55,000, giving a total of 112,000 tons, representing some 160,000 of oil of-vitriol; whilst the brimstone imported was close upon 118,000 tons, representing about 350,000 tons of O. V.; or, again, more than double that equivalent to the pyrites used ('Mineral Resources of the United States,' Calendar, 1886).

—	Spanish and Portuguese			Norwegian		Irish (Wicklow)		Belgian	Cornish	West-phalian	French	
	Tharsis		San Domingo									
	Highly cupriferous	'Average'	'Masons'	First quality	Second quality	Richer ore from Avoca	'Average'	—	Eight varieties	Meggen	Chessy and Sain-Bel (Lyons)	
Analyst	Pattinson	Alder Wright	Claudet	McCulloch	McCulloch	Pattinson	Alder Wright	McCulloch	Clapham	Pattinson	Mène	Scheurer-Kestner
Sulphur	49·30	49·07	49·00	46·15	38·17	44·20	30·84	45·60	24·0 to 34·9	45·60	45·2 to 47·6	45 to 48
Iron	41·41	44·28	43·55	44·20	32·80	40·52	—	38·52	27·1 ,, 60·7	38·52	39·0 ,, 39·7	—
Copper	5·81	2·75	3·20	1·20	1·10	·90	1·29	nil	·4 ,, 4·6	—	— —	1 to 2
Lead	·66	—	·93	—	—	1·50	—	—	0 ,, 7·4	·64	— —	—
Zinc	trace	—	·35	2·10	2·32	3·51	—	6·00	0 ,, 9·0	6·00	— —	—
Arsenic	·31	·38	·47	nil	trace	·33	—	trace	0 ,, 1·2	trace	present	—
Lime	·14	—	·10	2·55*	11·90*	·24	—	·11*	0 ,, 3·6*	·11	— —	—
Silica and insoluble matter	2·00	3·52	·63	3·20	12·20	8·80	—	9·00	2 ,, 38·7	8·70	9·6 to 11·0	—
Alumina, magnesia, oxygen, moisture, and matters not especially determined	0·37		1·77	·60	1·51	·34	—	·77	—	·73	3·9 ,, 4·8	—
	100·00	100·00	100·00	100·00	100·00	100·34	—	100·00	—	100·30	— —	—

* Carbonate of lime.

For pyrites about ·5 grm. is treated with about 10 c.c. of a mixture of 3 vols. nitric acid (sp.gr. 1·4) and 1 of strong hydrochloric acid, both perfectly free from sulphuric acid, solution being accelerated by heating now and then; the whole is evaporated to dryness on the water-bath, evaporated again after addition of 5 c.c. more hydrochloric acid, and the residue taken up with 1 c.c. of strong hydrochloric acid and 100 of water. The filtrate is treated with ammonia in only slight excess, filtered, and washed, and if the total fluid exceeds 200 c.c. is concentrated by evaporation. Finally, a very slight excess of pure hydrochloric acid is added, the whole heated to boiling, and about 20 c.c. of a 10 p.c. solution of barium chloride (also heated to boiling) added. The precipitate is allowed to stand for half-an-hour, the clear portion run off through a filter, and the residue treated with 100 c.c. of boiling water and allowed to settle two or three minutes, the supernatant liquid being then run off through the filter, and the precipitate similarly washed by decantation three or four times. Operating in this way, any sulphur present as galena or heavy spar (valueless for vitriol-making) is not included in the percentage ultimately found.

In the case of burnt cinders, where sharp accuracy is less necessary, the material is dissolved in aqua regia and evaporated, and the residue taken up with hydrochloric acid and water, and precipitated as above by barium chloride at a boiling heat, the removal of iron by ammonia being omitted.

J. Watson finds (S. C. I. 1888, 305) that a simple and expeditious process for determining sulphur in burnt pyrites may be based on Pelouze's method of sulphur estimation—viz. cautious fusion with sodium carbonate and potassium chlorate, and titration of the alkali not converted into sulphate. The chlorate is omitted, the burnt ore being mixed with a known quantity of sodium bicarbonate and heated over a rather low Bunsen flame for 5–10 minutes. The mass is then cautiously stirred with a wire stirrer, and the heat increased for 10–15 minutes more, when the oxidation of the sulphur is complete. Finally the mass is treated with water, and the unneutralised soda titrated with standard acid, using methyl orange as indicator.

Lunge has investigated this method (Zeit. f. angew. Chem. 1889, 239; S. C. I. 1889, 572), and finds that it is not only the simplest and cheapest, but also the quickest and most accurate, test yet devised for the purpose; and, after additional experience of it, states (S. C. I. 1890, 1014) that it was found to be preferable to all other methods tried in his laboratory.

Jannasch and Richards (J. pr. 39, 321; S. C. I. 1889, 819) have carried out a series of experiments on sulphur determination in pyrites and similar minerals, and conclude that when the sulphur is determined by oxidation in the wet way and precipitation with barium salts, without removing iron first, a deficiency of 1–2 p.c. is apt to be occasioned by reason of the solubility of barium sulphate in solutions of iron salts; whilst, on the other hand, a small quantity of ferric oxide is present in the ignited precipitate, which they regard as due to the precipitation of a double sulphate of iron and barium.

Lunge (Zeit. f. angew. Chem. 1889, 473; see also C. J. Abs. 1890, 413 and S. C. I. 1889, 966) finds that in using the process of the 'Alkali Makers' Pocket-Book' (*supra*) the precipitated ferric oxide may carry down with it some basic iron sulphate if the liquid be boiled until the smell of ammonia is all but gone; but if the directions given are properly followed (a slight but distinct excess of ammonia to be added, warming for a few minutes till the precipitate settles, and filtering at once) no such loss of sulphuric acid occurs.

Jannasch (J. pr. 1890, 41, 566) determines the sulphur in pyrites by burning in a boat in a combustion tube in a stream of oxygen, receiving the products of combustion in bromine water.

4. **Plant used in vitriol-making.** While considerable differences still exist between the apparatus employed by different manufacturers in different countries, some works being far less complete than others in this respect, and whilst certain stages of the process admit, under varying conditions, of considerable variety of treatment, there are, nevertheless, certain fundamental features common to all vitriol-making plant; the essential characteristic being that by the combustion of sulphur (either free, as brimstone, or combined with metals, &c., as sulphides) in presence of excess of air, a mixture of sulphur dioxide, oxygen, and nitrogen is formed, which is then intermingled with certain gaseous nitrogen oxides and steam, the former only in relatively small quantities. Under these circumstances the nitrogen oxides act as 'carriers' of oxygen—*i.e.* they cause, in virtue of certain reactions in which they take part, a cycle of changes to occur, the end result of which is that oxygen becomes added on to sulphur dioxide and steam, forming sulphuric acid, thus: $2SO_2 + O_2 + 2H_2O = 2H_2SO_4$, whilst the nitrogen oxides are left in the same condition as at first, so that they react over and over again in the same fashion with successive quantities of sulphur dioxide, thus causing the formation of large amounts of vitriol relatively to their own mass. The nature of the intermediate reactions taking place in this cycle of changes is differently viewed by different chemists, whose opinions will be more conveniently discussed later on (*v.* p. 726).

The plant employed in the process consists essentially of (1) a burner, wherein the mixture of sulphur dioxide, oxygen, and nitrogen is formed; (2) an arrangement whereby the nitrogen oxides are added to the gases; (3) a steam generator, from which a current of steam can be further blown in; and (4) a capacious vessel, or series of vessels, or 'chambers,' in which the gases can react at leisure on one another, the sulphuric acid depositing therein in the liquid form, and the spent gases emerging at the far end of the chamber. This much is common to all vitriol plant, supplementary appliances now generally, though not universally, employed being the 'Gay-Lussac' tower, which is essentially a scrubber through which the exit gases are passed, and down which moderately strong sulphuric acid passes, so as to absorb nitrous fumes; and the 'Glover' tower, which is essentially another scrubber, placed between the burners and the chambers, through which the hot burner gases pass, whilst the nitrous vitriol from the Gay-Lussac tower, together with the somewhat dilute acid which precipitates in the chambers are made to flow down the tower; the result of which is, firstly, that the nitrous fumes dissolved both in the chamber acid and in the Gay-Lussac tower liquor are volatilised and brought back again into the stream of gases, and so used over again and yet again; secondly, that much water is evaporated from the weaker chamber acid, thus not only concentrating it without material expense, but also saving fuel by diminishing the amount of steam required to be blown into the chambers; and, thirdly, that a considerable fraction of sulphur dioxide is converted into vitriol in the tower itself, thus diminishing the amount of chamber space requisite for the chemical reactions.

Pyrites burners.—Although some amount of vitriol is still made from brimstone, and some from the gases obtained during the preliminary roasting of certain zinc, copper, and other valuable metallic ores in the process of smelting them, and by burning the sulphur-impregnated spent iron oxide of the gasworks, and such like materials, still by far the largest proportion manufactured in Europe is prepared from pyrites containing quantities of copper too small for extraction by the ordinary smelting processes, although usually large enough to be profitably extracted by the 'wet' method. Such pyrites as imported is mostly in somewhat large fragments, which are first of all broken up by hand or crushing machines and sifted, whereby two kinds of material are obtained, which require somewhat different treatment. The smaller quantity is the 'smalls,' including not only dust but also all fragments capable of passing through a $\frac{1}{4}$-inch or even a $\frac{1}{2}$-inch riddle; whilst the 'lumps' constitute the remainder, the largest being capable of passing through a 2-inch, or at most a 3-inch, screen (occasionally 'peas' are sifted out from the smalls, and treated separately from the finer dust and grains). The burner for lumps is generally known as the 'kiln,' from its general similarity to a miniature lime-kiln. The older forms of kiln consisted of a nearly square brickwork vertical tube 3 or 4 feet high with air-holes to facilitate combustion, a charging orifice at the top, and two openings at the bottom for the withdrawal of the burnt cinder, the gases produced passing away through a flue, provided with a damper for regulating the draught, and containing a nitre pot. This form of burner is fairly well suited to the combustion of poor ores requiring a pretty long column of material; but for the richer class of cupreous ores, now chiefly employed, a much less deep layer of ore is required, whilst the base is usually provided with horizontal firebars, between which the cinder drops out into an ashpit beneath: these are square-headed, but oval, square, or oblong in section, so that on rotating them by means of a long lever-key fitting on to the heads, the lumps of pyrites lying between them are gradually forced out. According to the relative positions of the bars, the air-space between them varies, to avoid which a helical thread on the bars is adopted by Helbig, the bars in all cases being rounded on those parts which rest on their supports, which are grooved, so that whilst each firebar can rotate on its longitudinal axis lateral motion is impossible. To avoid undue access of air, the ends of the bars are boxed in and doors provided, closed when the bars are not being turned; and to diminish the time during which the ashpit door is open for the removal of cinders a 'bogie,' or truck, is arranged in the pit into which the cinders fall, the removal of which is thus accomplished in a fraction of the time requisite for raking or shovelling them out.

Burners of a variety of different sizes and patterns are in use in different countries and districts; those mostly employed for Spanish ores in Britain are generally built in a double row, back to back, with a double common flue for the whole series built centrally along the row on the top of the back portion of each kiln, which plays into the flue through an orifice for the purpose, the nitre-pots being generally placed in an 'oven,' or expansion of the flue, at the end of the series. The fronts are cased in with stout iron castings, to which the various doors (sliding or hinged) for charging, stirring up to avoid or break up scars, working and rotating the bars, &c., are fixed as nearly airtight as may be, charging being effected through doors in front at the top part of the casing. The whole is well tied together with plates and rods, to avoid any formation of cracks and crevices by settling or expansion, &c. The air requisite for combustion is admitted partly through the unavoidable chinks between the doors and their settings, partly through various holes in the doors provided for the purpose, closed when required by inserting plugs or fragments of brick or burnt ore, &c. The internal portion is built of firebrick, with a slight 'batter,' or slope, downwards, so that the horizontal section is smaller in area at the level of the firebars than at that of the charging-doors, the internal cavity being shaped like an inverted square or oblong truncated pyramid. As regards dimensions considerable diversities occur in practice, some few manufacturers still adhering to the comparatively small-sized burners mainly in vogue twenty or thirty years ago (some 33 inches wide and 26 deep at the firebars and 42 inches square at the level of the bottom of the charging-door, giving a total 'batter' of 6 inches back and front and 9 inches sideways); others using slightly larger sizes (some 39 inches wide, and 42 deep at the bars, and 48 by 51 at the charging-door, giving a total 'batter' of 9 inches both ways); but most employing larger sizes still, up to 54 inches wide and 60 to 66 deep at the bars. The smallest sizes thus represent areas of 8·25 square feet at the bars and 12·25 at the charging doors, giving a mean area of 10·25 square feet. These kilns will readily burn 4 cwt. of Spanish ore in 24 hours, or about 44 lbs. per square foot of mean area, without danger of fritting the lumps together, if due attention be given; but are often worked much more heavily, in which case 'scarring,' or fluxing of the ore, is apt to occur pretty frequently unless great care is bestowed. The largest sizes, on the other hand, possess a mean area of something like 25 square feet, and when worked with charges of 7 cwt. and upwards per 24 hours give a rate of burning of 31 lbs. and upwards per square foot of mean area. The most frequently employed dimensions are probably kilns of somewhere about 16 to 18 square feet firebar surface and 22 to 24 square feet area at base of charging-doors, giving a mean area of 19 to 21 square feet, representing (when burning 7 cwt. daily) 37 to 41 lbs. of ore per square foot of mean area for 24 hours. This rate of burning is probably near the maximum consistent with proper freedom from fluxing, and thorough combustion (as far as practicable) of sulphur, when ores of the Spanish and Portuguese class are employed; but if poorer ores are used much more rapid rates of burning (relatively to the weight of ore passed through the burner in a given time) may be safely employed. Thus Lunge states, on the authority of various observers, that, whilst in England the quantity of 48 p.c. pyrites burnt daily rarely exceeds 40 lbs. per square foot of grate-surface (about 35 per square foot of mean area), in German works, using Westphalian pyrites containing 40–42 p.c. of sulphur, quantities up to 64 lbs. per square foot of grate-surface (say 55 lbs. per square foot of mean area) can be safely burnt; whilst with Valois ore, containing only 35 p.c. of sulphur, quantities can be burnt daily up to 92 lbs. per square foot of grate-surface (say 80 lbs. per square foot of mean area).

When the kilns are working properly the great majority of the oxidation takes place before the fragments have sunk many inches, and the rest is practically effected in the middle of the kiln; so that by the time the burnt ore reaches the firebars it has become all but cold through the chilling action of the entering air. If the temperature at this level is perceptibly raised, the burner is not in proper working condition, either through being partly stopped up by dust or scarring, or by overcharging or insufficient draught. On the other hand, with too great an air-supply the burner becomes chilled, so that the fresh charges do not ignite properly, whilst the gases produced are too much diluted with excess of air. Should the temperature rise too high in the zone where the chief combustion takes place, 'scars' or 'scours' are apt to be formed through the fritting of the lumps together.[1] When the fluxing takes place to too great an extent to permit of the lumps being broken up by the insertion of stout iron bars used as pokers, great inconvenience is caused, it being necessary in bad cases to shut off the affected kiln from the rest of the series, and more or less unbuild it so as to remove the obstructing mass. This inconvenience is less likely to be brought about with poorer ores containing slate or difficultly fusible gangue than with richer ores containing little but metallic sulphides, wherefore the layer of lumps is made considerably less in vertical height when such ores as the Spanish and Portuguese cupreous pyrites are burnt than when poorer slaty ores, like Wicklow pyrites, are employed. From 28 to 30 inches as a maximum, down to 22 to 24 as a minimum, thickness of layer, with an average of about 27, are usual figures in the first case; whilst layers 40, or even 48, inches thick can often be safely used with slaty ores, and are indeed necessary on account of the slower rate of combustion. Even then it frequently happens that sufficient air for complete oxidation does not reach the interior of the larger lumps, so that on breaking them after passing through the kiln cores still 'green' or unburnt are distinctly visible; whence, of course, a higher percentage of sulphur is lost through defective combustion than with ores oxidising more readily. The following figures, obtained by the author some few years ago in a works where both Wicklow ore and Spanish pyrites were used, illustrate this point, the percentages representing the mean amounts of unburnt sulphur present in quantities representing several thousands of tons of burnt ore of both classes made during periods of several months each:—

	Wicklow ore	Spanish ore
Cwts. of pyrites per kiln per 24 hours . .	9·81	7·25
Mean percentage of sulphur in burnt ore .	6·06	3·05

In the same way the following figures were obtained, showing the result of increased 'duty' with kilns burning Spanish ore in producing a perceptible though small increase in the average amount of unburnt sulphur contained in the cinders.

Cwts. of pyrites per kiln per 24 hours	Percentage of sulphur in cinders
5·8	2·85
6·8	2·88
7·0	3·01
7·5	3·08

As regards the Wicklow and Spanish ores, the above figures are fairly typical of the general experience of vitriol-makers in the matter, and readily explain why poor ores have so largely fallen into disuse; for obviously, for the same quantity of sulphur actually burnt a much larger amount of poor ore must be consumed than corresponds simply to the lower percentage of sulphur contained therein. Thus, 100 parts of Spanish ore containing 48 of sulphur yielded, say, 70 of cinders, containing 3·05 p.c. of sulphur, wherefore $48 - \cdot 7 \times 3\cdot 05 = 45\cdot 86$ parts of the original sulphur were burnt; whereas 100 parts of poor ore containing about 32 p.c. of sulphur (and therefore $\frac{2}{3}$ as much as the Spanish ore) yielded, say, 80 parts of cinder, containing 6·06 p.c. of sulphur, wherefore only $32 - \cdot 8 \times 6\cdot 06 = 27\cdot 15$ parts of the original sulphur were burnt. So that, instead of requiring $\frac{3}{2}$ as much of the poorer ore to produce a given amount of sulphurous acid as would be required of the richer ore, the proportion was $\frac{45\cdot 86}{27\cdot 15}$, *i.e.* 169 p.c. instead of 150. When it is further remembered that the charges for carriage, breaking up, and labour generally in burning each kind of ore will not differ widely for equal weights, it is at once evident that a given quantity of sulphur is practically of much more value in a rich ore than in a poor ore; so that if the price per unit of sulphur is the same, the richer ore is considerably the cheaper. Apart from this consideration, moreover, poorer ores usually give burner gases averaging smaller percentage contents of sulphur dioxide, thus rendering larger amounts of chamber space requisite in proportion to the sulphur burnt—*i.e.* diminishing the output obtainable from a given size of plant (*vide* pp. 725 and 736 *et seq.*).

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[1] With a limited supply of air the first action of heat on iron disulphide is to burn off one-half of the sulphur present, leaving comparatively easily fusible ferrous sulphide FeS.

Even with the richest ores it is never practicable to burn off the sulphur completely on the large scale, partly because the copper present has a tendency to creep into the centre of each lump, forming a 'kernel' of copper-iron sulphide which does not oxidise rapidly, and partly because highly basic ferric sulphate is apt to be formed in small quantity. For the subsequent process of extraction of copper by the wet method, it is desirable that the sulphur left should be at least not less than the copper present, and preferably $1\frac{1}{2}$ to 2 times as much, green smalls being required to be added to the burnt ore when burnt too low to bring up the total sulphur percentage to the necessary amount. In some works 3 to 3·25 p.c. of sulphur is the average amount left in the burnt ore when Spanish pyrites is used; in others somewhat higher averages—3·5 and even 4 p.c.—but rarely, if ever, is the average amount for any considerable period below 2·75 p.c., although of course it may well happen that particular batches fall considerably below this limit. Admitting that 100 parts of ore containing 48 p.c. of sulphur yield 70 parts of cinder containing 3·5 p.c., the quantity of sulphur left in the burnt ore represents $\cdot 7 \times 3\cdot 5 = 2\cdot 45$ per 100 of original pyrites, and therefore $\frac{2\cdot 45}{48} = 5\cdot 10$ p.c. of the sulphur contained therein. Something like 95 p.c. of the sulphur contained in the pyrites is therefore usually burnt off and escapes in the gases from kilns consuming Spanish ore, and somewhat smaller proportions when poorer ores are employed.

Whatever the kind of ore burnt, a most important feature of the process is the due admission of air in adequate quantity, not only to completely burn all sulphur and prevent volatilisation thereof in an unburnt state, but also to furnish the oxygen required for the formation of vitriol by the further oxidation of sulphur dioxide in the chamber, without unduly diluting the total mass of gases by permitting too large an excess of air to be present. To effect this requires considerable address and experience, the precise manipulation requisite and the indications of proper working varying more or less with each kind of ore. To prevent undue access of air, the ashpit below the firebars is closed in with doors fitting all but air-tight, as similarly are the ends of the firebars, the stirring-holes, and the charging-doors, these being partly opened as required so as to let in just the required proportion of air; preferably, smaller holes are drilled in the doors, more especially those closing in the ashpit, and closed up as required by the insertion of plugs, or fragments of cinder &c. In order to keep up as near an approach to uniformity as possible in the character of the gases evolved from the set of kilns, each burner is re-charged at equidistant intervals of time in regular rotation—*i.e.* a set of 12 burners working a 24 hours turn would be so treated that the second was re-charged two hours after the first, the third two hours later, and so on through the series; excepting when extremely large burners are used requiring slower burning, and therefore re-charged only once in 24 hours, re-charging every 12 hours is the period most frequently adopted. As a check upon the working of the burners so far as admission of air is concerned, analyses made from time to time of the gases escaping at the far end of the chambers are of great importance, inasmuch as from the percentage of oxygen found therein after absorption of all sulphur compounds and nitrogen oxides exact knowledge is gained of the average amount of surplus air admitted during burning and re-charging &c. (*v.* p. 734).

Burners for smalls. A large number of forms of burner for this purpose have been invented, one of the earliest of which is Spence's furnace, sometimes known locally as a 'gimcrack,' in principle very much like a closed salt cake roaster. The flame from a coal fire plays through longitudinal flues under the sole of the roaster, thereby communicating auxiliary heat and facilitating the oxidation. From time to time the layer of smalls placed on the sole is stirred up by rabbles introduced through the working doors, the sulphurous gases produced passing off to the chambers through a flue. Fresh smalls are introduced from time to time at the far end, and gradually raked towards the fire end, where the spent dust is withdrawn. Latterly this class of furnace has been largely superseded by arrangements requiring no extraneous heat furnished by coal &c. One of the simplest of these consists of a pair of shelves arranged over the mass of burning pyrites in an ordinary kiln so as to be heated thereby. These consist of iron or preferably fireclay slabs built into the brickwork, and provided with flanges at the edges to prevent the smalls falling into the kiln and choking the draught. The results obtained with this arrangement have generally been considered satisfactory; but, according to Lunge, the dust is never perfectly burnt, and much surplus air is unavoidably introduced when doors are opened to stir the smalls or withdraw or re-charge them. An improved form has been introduced by Hasenclever and Helbig, the smalls being burnt on a series of alternate sloping shelves, arranged one above the other in a square tower, up which the gases from an ordinary kiln pass in such fashion as to flow over each layer of smalls in alternate directions. The slope of each shelf is 38°, or slightly more than the natural slope of pyrites fragments, 33°; so that on removal of cinder at the base of the lower shelf (by a hand-rake or a wheel worked by machinery) the particles slide gradually down that shelf, and consequently down all the others, somewhat as sand flows down the funnel of an hourglass in action. A variety of other forms of burner have been devised in which the heat of combustion of the smalls alone is sufficient, so that no lump pyrites at all is requisite. Fig. 2 represents a section of a burner of this class introduced by Malétra, and modified by Schaeffner, the smalls here passing gradually downwards from one to another of a series of horizontal alternate shelves. In MacDougall's mechanical furnace the pyrites is continually introduced at the top by an elevator, and raked by a series of arms affixed to a vertical spindle from one to another of a set of superposed shelves, the pallets of the rakes being so arranged that they cause the smalls to pass from the centre to the circumference of one shelf, from which they fall on to the one below, and from the circumference to the centre of that one from which they fall on to the next lower one, and so on alternately down the series until they escape completely burnt at the bottom. P. Spence patented in 1878 a variety of shelf burner provided with a mechanical stirring arrangement, which has been used with success in America (Lunge). In all burners of this kind, and, indeed, in all cases where fine smalls are burnt under any circumstances, a much larger amount of dust is carried off with the escaping gases than is the case with kilns; accordingly a dust-depositing chamber of some kind, usually a large expansion of the flue with or without baffle plates disposed in various ways, is generally provided to diminish the large amount of contamination of the vitriol that would otherwise be brought about. Even with kilns only this is a useful precaution, especially when a Glover tower is used; when this is not the case the dust is generally sufficiently deposited in the cooling flues interposed between the burners and the chambers. The 'flue dust' thus collected is removed from time to time; in character it necessarily varies much, sometimes being practically nothing but fine particles of burnt ore mechanically carried along by the gases, and sometimes containing large quantities of substances sublimed from the burning mass, more especially arsenious oxide, which sometimes constitutes more than half of the deposit. Sublimed unburnt sulphur, mercury, and oxides &c., of lead, zinc, selenium, and thallium &c., are also constituents, according to the nature of the ore burnt. Ardèche pyrites contains fluorspar in sufficient quantity to form enough hydrofluoric acid vapour to cause serious injury by corrosion to glass apparatus used for distributing nitric acid in the chambers.

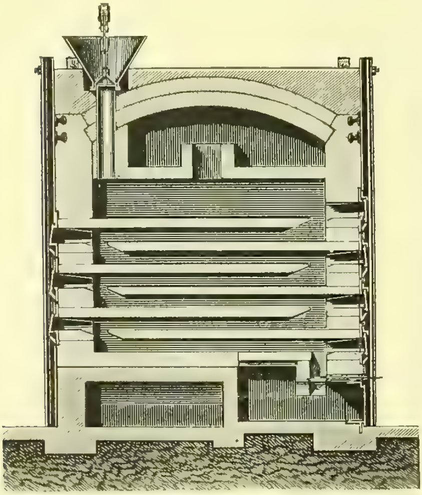

Fig. 2.

W. Crowder gives the following figures as the average of a large number of daily tests of the sulphur contained in the partly-burnt smalls on each of the seven beds of a kiln, arranged on the Malétra and Schaeffner principle (*supra*), the original smalls containing 50 p.c. of sulphur, and the kilns being charged every eight hours, so that the smalls remain in the kilns 56 hours whilst passing from shelf to shelf (S. C. I. 1891, 295):

	November (23 tests)	December (26 tests)
No. 1 shelf	32·27	32·81
„ 2 „	21·41	17·55
„ 3 „	12·77	11·09
„ 4 „	6·39	5·03
„ 5 „	4·08	3·42
„ 6 „	2·35	2·56
„ 7 „	2·27	1·96

The gases thus produced (drawn from the flues before reaching the nitre stack) contained 6·03–7·02 p.c. of SO_2, and 9·27–10·00 p.c. of oxygen, by volume in one (old) set of dust-kilns; and 4·86–7·03 p.c. of SO_2, and 8·90–10·68 p.c. of oxygen in another (new) set; whilst the burner-gas from lump ore kilns contained 4·97–6·63 p.c. of SO_2, and 9·60–11·21 p.c. of oxygen. The temperature of the gases from the smalls burner was usually near 610°F. (sometimes as low as 570°F., and sometimes above 620°); whilst that from lump kilns was between 773° and 800°F., or about 180°F. (=100°C.) higher.

In Britain, where the bulk of the pyrites burnt is of Spanish and Portuguese origin, the use of smalls burners is mainly confined to the working up of the dust of the pyrites produced in transport and during breaking up; and in these cases it is often found inconvenient to combine the current of gases from the smalls burners with that from the kilns into one flue, on account of inequalities of draught thereby rendered imminent. Frequently the use of a separate smalls burner is rendered unnecessary by making balls or cakes of the smalls moistened with water and ground up, and then dried on the roof of the kilns or flues; incipient oxidation is thus brought about, in consequence of which the mass binds together in lumps sufficiently hard to burn in the ordinary pyrites kilns along with the fragments of broken-up ore. Formerly balls were made by mixing the smalls with clay and drying; but this method of treatment has now mostly gone out of use, as the clay interferes with the proper burning of the ball as well as with the subsequent copper extraction. In some cases, however, pyrites smalls, purchased as such, obtained from mines of various kinds, are used exclusively or nearly so as sources of sulphur dioxide; or the analogous sulphide of zinc (blende) or copper matts (sulphides) obtained during the process of copper smelting are roasted, and the gases produced utilised for vitriol-making. For these purposes Spence's furnace, more or less modified as occasion may require, is generally employed in Britain; but on the Continent one or other of the various forms of shelf burner &c. are usually preferred; the working up of such materials into vitriol as an adjunct to the main smelting operation is there more frequently carried out than here, wherefore the greater attention paid to improvements in burners intended for such special purposes.

A somewhat analogous material is the 'spent oxide' of the gasworks—*i.e.* a mixture of iron oxide and sulphur &c. formed during the purification of coal-gas from sulphuretted hydrogen by 'bog-iron ore' (hydrated ferric oxide). During the first action sulphur is deposited and ferrous sulphide and water formed, thus :

$$6H_2S + 2Fe_2O_3 = 4FeS + 6H_2O + S_2,$$

and on exposing the mass to the air to 'revivify' it more sulphur is formed and ferric oxide reproduced by absorption of oxygen, thus :

$$4FeS + 3O_2 = 2Fe_2O_3 + 2S_2.$$

After using a certain number of times the action on sulphuretted hydrogen of the mass becomes too languid to be of service; the substance is then employed either as a source of artificial brimstone, or directly burnt to produce vitriol in kilns analogous to those employed for pyrites smalls, such as Hill's, closely akin to the Malétra shelf burner.

Brimstone burners. In the simplest form of burner, the brimstone is introduced from time to time through a door on to an iron tray, the hinder part of which is cooled by an air channel underneath, to diminish the tendency to sublimation of unburnt sulphur. The nitre pots are simply placed on the sole in the midst of the blazing sulphur. In another form the brimstone is introduced through a door, and burnt on a tray, the fumes passing through an orifice into an upper chamber, divided into two by a midwall, so that the gases pass from front to back in the lower half, from back to front in the first half of the upper chamber, thence through to the other half, and so from front to back again to the flue, which is common to two adjacent burners. In Harrison Blair's burner the brimstone is introduced through a charging door on to the sole, whence the gases pass into a serpentine passage, into which air is admitted so as to burn the sulphur volatilised without complete combustion; the gases then pass to a second storey, where they heat the nitre-pots, and thence into a cooling dome, and so to the flue. By duly regulating the air supply the burner gases can be obtained of suitable concentration, and at a high enough temperature to work a Glover tower when the burner is working to its full capacity, some 4 tons daily; or the consumption can be reduced to one-fifth the quantity. When a Glover tower is not used, a long cooling pipe is necessary before the gases are admitted into the chamber.

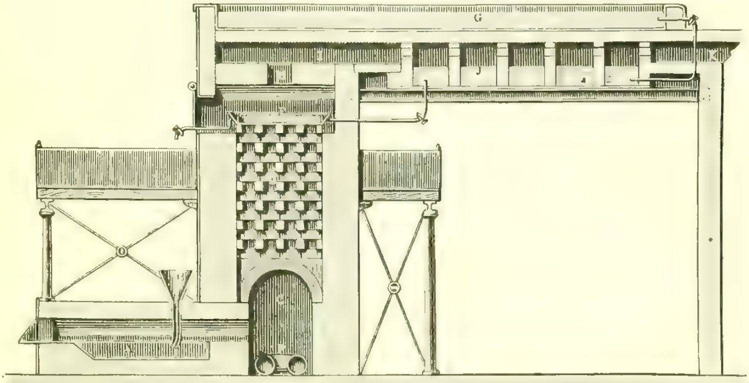

FIG. 3.

Fig. 3 represents Glover's brimstone burner. A is the burner plate fed by the hopper, B ; C is a chamber the upper part of which is filled with loosely-stacked bricks, D, into which air is admitted by the pipes F to complete the combustion of the sulphur; E is a platinum dish, and J, G leaden pans for concentrating the acid ; K, flue to Glover tower.

When smalls burners are employed it is usual to equalise as much as possible the current of gases produced by charging several burners in rotation at regular intervals; the door being opened, the ashes are raked out, and a fresh charge introduced as rapidly as possible. Much surplus air necessarily finds its way into the chamber during this operation, wherefore charging through a hopper is preferable when practicable. Petrie has attempted to make a continuous feed burner; but the peculiar behaviour of melted sulphur on further heating in becoming thick and viscid prevents this kind of arrangement answering well, a regular flow of brimstone being virtually impracticable. Hemptinne supplies liquid brimstone to the burner plates from a cast-iron box divided into compartments built into the front wall. Perpendicular partitions, reaching nearly but not quite to the bottom, prevent the burner gas blowing out in front.

Sulphuretted hydrogen as a source of vitriol. Although many attempts have been made at various times to utilise sulphuretted hydrogen (obtained from alkali waste, galena by the action of hydrochloric acid in the manufacture of oxychloride of lead, ammoniacal gas liquor, &c.) for the production of vitriol, yet so many practical difficulties were encountered (chiefly in obtaining the gas sufficiently pure and regularly supplied for proper combustion) that almost invariably the process was abandoned in favour of the production instead of artificial brimstone. The most successful way of dealing with sulphuretted hydrogen as a source of vitriol appears to have been the passing of the gas through an ordinary pyrites kiln so as to effect its combustion with little or no cost; the gas evolved from galena by the action of hydrochloric acid (not containing any carbon dioxide) has been thus dealt with, with very satisfactory results. One of the most recent of the processes whereby brimstone is obtained—that of Claus—consists in mixing with the sulphuretted hydrogen a proportion of air just sufficient to form water by uniting with the hydrogen present without containing any surplus oxygen, and passing the mixture through a bed of hot ferric oxide, whereby a mixture of nitrogen, steam, and sulphur vapour results, from which brimstone or flowers of sulphur can be obtained by cooling. Messrs. Chance Brothers have successfully applied this process to the regeneration of brimstone from alkali waste by means of the impure carbonic acid obtained in calcining limestone (S. C. I. 1888, 162), this gas being forced through a succession of vessels containing alkali waste and enough water to make a creamy paste. In the earlier of the series sulphuretted hydrogen is evolved and calcium carbonate formed; in the later ones the sulphuretted hydrogen is absorbed so as to form calcium hydrosulphide. By charging the members of the series in rotation, and suitably altering the connections, the process is divided into two alternate phases, in the first of which the sulphuretted hydrogen evolved in the earlier vessels is practically wholly absorbed by fresh alkali waste, little but the nitrogen of the limekiln gases passing off; whilst in the second phase the calcium hydrosulphide thus formed is decomposed by fresh limekiln gases evolving sulphuretted hydrogen in virtue of the reaction:

$$CaH_2S_2 + H_2O + CO_2 = CaCO_3 + 2H_2S.$$

In this way a gas rich enough in sulphuretted hydrogen to burn freely and continuously is produced in the alternate intervals of second phase, and is led away to a gas-holder (contact with water being prevented by a layer of 'dead oil'), from which it passes off in a regular stream to the Claus kiln. About 33 to 34 p.c. of sulphuretted hydrogen, 1·5 to 2 of carbon dioxide, and 65 of nitrogen, represents the average composition of the gas thus stored in the gas-holder. The comparative uniformity of composition thus attained, the increased richness in sulphuretted hydrogen, and the regularity of the supply enable the gas to be successfully employed in the manufacture of pure sulphuric acid, it being simply requisite to burn the gas along with a surplus of air, the combustion taking place as readily as that of coal-gas. The heat thus produced is sufficient not merely to work a Glover tower between the burners and chambers, but also to concentrate acid in a pan on the top of the kiln; it is stated by Chance that from 98 to 99 p.c. of the sulphur thus burnt can be obtained in the form of chamber acid when Gay-Lussac and Glover towers are used, the difficulties inherent in the former methods of utilising sulphuretted hydrogen chiefly due to irregularity of supply being obviated very thoroughly, and no more than the usual quantity of nitre (2·9 to 3·6 parts per 100 of sulphur burnt) being required. According to Lunge, in some works where the Chance process has been adopted an increased consumption of nitre has been noticed; this he attributes to irregularity in the composition of the gas, and notably to the presence of carbon dioxide therein. On the other hand, in other works a diminution in nitre consumption has been effected, owing to the absence of fluctuations in the character of the burner gas, a matter more difficult to insure with pyrites burners.

Burner gases. The production of a mixture of gases suitable for vitriol-making by burning sulphur, metallic sulphides, or sulphuretted hydrogen in air, is not quite as simple an operation as would at first sight appear. In the first place the action of hot air on sulphur is not only to form sulphur dioxide, but also more or less trioxide, according to the way in which the process is carried out, the surface action of the vessels employed being doubtless largely concerned in the change (*vide*, p. 713). In the case of metallic ores, not only is this surface action largely manifested, more especially in the case of pyrites, but further there is more or less tendency for the metallic sulphide to take up oxygen directly, forming (basic) sulphate which suffers decomposition by heat, evolving SO_3 as in the Nordhausen acid manufacture. Hence it results that pyrites burner gases generally contain notably larger proportions of SO_3 than brimstone burner gases. When the gases are not led immediately through a Glover tower, the sulphur trioxide and the moisture present in the air feeding the burners often condense together as vitriol in the cooling pipes leading the gases to the chambers, so that a pretty strong acid often drips from these pipes (usually this is collected and employed in the nitre-pots or otherwise). Nextly, the volume of air requisite for complete combustion of sulphur is by no means the same whether the sulphur be free as brimstone or combined with a metal or with hydrogen. Thus for free sulphur, pyrites, zinc sulphide, and sulphuretted hydrogen, the following equations represent the main changes taking place respectively:

$$S + O_2 = SO_2$$
$$4FeS_2 + 11O_2 = 8SO_2 + Fe_2O_3$$
$$2ZnS + 3O_2 = 2SO_2 + 2ZnO$$
$$2H_2S + 3O_2 = 2SO_2 + 2H_2O$$

which indicate that for a given weight of sulphur converted into SO_2 in each case, quantities of oxygen, and therefore of air, will be requisite in the proportion of 8, 11, 12, and 12 respectively; and consequently that if only sufficient air be used to complete the combustion, or if equal quantities of sulphur and air be employed in each case respectively, the resulting gases will be richest in sulphur dioxide when brimstone is burnt, and poorest when zinc sulphide or sulphuretted hydrogen is burnt. In actual practice it is always indispensable to use an excess of air larger than that required to convert SO_2 into vitriol, not only to avoid sublimation of sulphur which might otherwise more often take place through deficient oxidation, but also to facilitate and intensify the carrier action of the oxides of nitrogen, which up to a certain extent act the more rapidly the more free oxygen is present for them to react with. Admitting the same proportionate excess in each case, it obviously results that a larger volume of burner gases is produced for a given quantity of sulphur consumed when sulphuretted hydrogen and zinc oxide is burnt, than with pyrites, and with pyrites than with brimstone; *i.e.*, *cæteris paribus*, amounts of chamber space are requisite for a given consumption of sulphur in these forms in the same order. In the case of pyrites it is usually considered preferable to employ such a surplus of air as will, after all SO_2 is converted into vitriol, furnish a mixture of nitrogen and oxygen in the exit gases, containing from 5–8 p.c. of oxygen and 92–95 of nitrogen, which corresponds approximately with the following composition of burner gases (*vide* p. 735):

Nitrogen . . .	81·5 to	82
Oxygen . . .	10·5 „	9
Sulphur dioxide . .	8 „	9
	100·0	100

The admission of this excess of air can obviously be controlled by analytical examination of either the burner gases entering the chambers, or the exit gases leaving them; both methods are sometimes employed, but more frequently the latter only. When the sulphur dioxide present is to be determined, the gas is slowly aspirated through a solution containing a known quantity of iodine until the latter is rendered incapable of giving a blue colouration with starch, the volume of gases employed being regarded as equal to that of the water run out from the aspirator (Reich's method). The following table gives the relationship when the iodine taken is 10 c.c. of decinormal solution (12·7 grms. per litre) mixed with 50 c.c. of water and a little sodium hydrogen carbonate and starch paste, the volume of the aspirated gas being supposed to be previously reduced to 0°C. and 760 mm. (Hurter and Lunge, Alkali Makers' Pocket-book):—

Volume of gas aspirated	Percentage of SO_2 by volume	Volume of gas aspirated	Percentage of SO_2 by volume
82c.c.	12	128c.c.	8
86	11·5	138	7·5
90	11	148	7
95	10·5	160	6·5
100	10	175	6
106	9·5	192	5·5
113	9	212	5
120	8·5		

When the oxygen is to be determined, the gas to be examined is washed through caustic potash solution and treated with phosphorus, ammoniacal cuprous chloride, or alkaline solution of pyrogallol. A convenient form of gas analysis apparatus has been arranged by Orsat,[1] consisting of a gas burette holding 100 c.c. connected by a flexible tube with a reservoir of water, by raising or depressing which the gas is driven out from or sucked into the burette, which is surrounded by a water-jacket to diminish temperature fluctuations. Two laboratory vessels are provided, one containing caustic potash solution, and the other ammoniacal cuprous chloride solution. The measured volume of gas is passed into the former of these first, whereby the sulphur dioxide is absorbed; then measured again, and passed into the second, in which the oxygen is absorbed; and finally measured a third time; the diminutions in bulk between each consecutive pair of measurements thus indicating, with sufficient precision for technical work, in the course of a few minutes the sulphur dioxide and oxygen respectively present. Rods of phosphorus require several hours to effect a complete removal of oxygen. Alkaline solution of pyrogallol works rapidly, but under certain circumstances may evolve carbon monoxide, thus impairing the accuracy.

Lunge states (S. C. I. 1890, 1014) that when it is necessary to take into account the sulphur trioxide existing in burner gases, the above method is not applicable, since it only indicates the sulphur dioxide. By employing a dilute solution of caustic soda, with phenol phthaleïn as indicator, a sharp valuation is obtainable of the 'total acidity,' including sulphurous and sulphuric acids jointly.

Valuations by density estimation—such as those used in testing illuminating gas &c.—would be readily applicable for technical purposes were it practicable to construct a gas balance of material that would resist the action of the acid gases; and by such means a continuous diagram representation of the results might be obtained.

When bases, such as lime, are present in the pyrites used, more or less sulphate is formed and retained in the cinder, thus diminishing the richness in sulphur dioxide of the burner gases relatively to the air employed. When poor ores are used, it is, generally speaking, impracticable to obtain efficient combustion without the introduction of more air than corresponds with the most desirable proportion of surplus oxygen. Thus whilst with rich pyrites the burner gas with proper management may be made to average between 8 and 9 p.c. of SO_2 continuously, sensibly less rich gas is as a rule produced from poorer ores, 6 to 7 p.c., or even less, being nearer the average in such cases. The effect of this is to render a larger amount of chamber space requisite to hold the gases produced from a given amount of sulphur combustion—*i.e.* to diminish the amount of sulphuric acid that can be made in a given set of chambers with poorer ores as compared with richer ones; thus furnishing another reason, in addition to those already cited (p. 720), why a given quantity of sulphur in the form of a poor ore is practically far less valuable than the same quantity in the form of a richer ore. Coal-brasses (pyrites imbedded in coal) always contain enough carbonaceous matter, even after careful picking, to yield a notable admixture of carbonic acid in the gases. This is eminently objectionable, because the gases are thus diluted both by carbon dioxide and the nitrogen of the air used to form it. Moreover, the presence of carbon dioxide is generally believed to interfere in some way not clearly understood with the conversion of sulphur dioxide into vitriol.

Could oxygen be obtained at a sufficiently low price to permit of its being used instead of air to generate sulphur dioxide, the diluting effect of the nitrogen on the burner gases would be obviated, and very much smaller chambers required to produce the same make of acid; probably also less nitre would be required than at present. Hitherto, however, it has been found cheaper to prepare oxygen by decomposing sulphuric acid by heat (whereby sulphur dioxide and water are also produced) than to reverse the process; so that although the method has been proposed and even patented by more than one inventor, it has never been worked on a manufacturing scale for the production of vitriol, although attempts in this direction have been made for the preparation of sulphuric anhydride (*vide* p. 714).

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[1] Several other [illegible] nical purposes have [illegible] Younger, Hempel, Bunte, &

5. **Nitrogen oxides.** On account of the relatively larger cost of nitrogen oxides as compared with sulphur, it is always a desideratum to reduce the quantity of these indispensable reagents to the minimum possible consistent with efficient work; but from the nature of the chemical changes involved there is a limiting proportion between the quantity of nitrogen oxides contained in the gases and the sulphur burnt, beyond which the nitrous fumes cannot be reduced without so slackening the rate of conversion of sulphur dioxide into sulphuric acid as either to render a large increment in chamber space imperative (*i.e.* a diminution of output from a given plant), or else to cause great waste by deficient conversion and consequent loss of sulphur dioxide in the waste gases. The precise limiting value, of course, varies somewhat under different circumstances, the chief source of variation being the employment or otherwise of Gay-Lussac and Glover towers. When these are used, the great bulk of nitrous fumes contained in the exit gases, and dissolved in the chamber acid, is recovered and brought back again into the chambers. Were it not that certain secondary reactions occur which prevent the possibility of a given quantity of original nitrous fumes being recovered over and over again without other loss than that due to slightly imperfect recovery, the quantity of nitrogen oxides requisite to be continuously generated from fresh materials would be simply that equivalent to the imperfection of recovery; in actual practice, however, a considerably larger quantity than this of additional nitrous fumes is requisite to supply these sources of loss—*i.e.* to overcome the diminishing effect of certain secondary chemical changes which interfere with the completeness of the cycle of operations theoretically taking place. When Gay-Lussac and Glover towers are not used, a much larger proportion of constantly generated nitrous fumes is required to keep the chambers in proper working condition, on account of the non-recovery, usually about 2½ to 3½ times as much; *i.e.* from 2 to 4 parts of nitre per 100 of sulphur burnt with recovery as compared with 8 to 12 parts without.[1]

A large number of different views as to the nature of the normal chemical changes taking place in the vitriol chamber (as well as of those occurring under abnormal conditions) have been from time to time put forth by different observers; these may conveniently be divided into two classes according to the nature of the oxide of nitrogen regarded as playing the chief part in the carrier action taking place—one theory regarding nitric oxide, NO, as the essential agent, and the other considering nitrous anhydride, N_2O_3, to be the leading active body. A full discussion of all the different views based on one or other of these primary assumptions and their respective advantages and demerits is here impossible on account of limits of space; whichever oxide is regarded as the essential agent, it is practically obtained by exposing nitric acid, either in the liquid state as such, or as nascent vapour evolved from a mixture of nitre and sulphuric acid by heat, to the action of the hot burner gases, when reduction takes place in accordance with one or other of the equations

$$(1)\ 3SO_2 + 2NO_3H + 2H_2O = 3H_2SO_4 + 2NO.$$
$$(2)\ 2SO_2 + 2NO_3H + H_2O = 2H_2SO_4 + N_2O_3.$$

Assuming *nitric oxide* to be the main active carrying agent, the cycle of changes taking place over and over again in the vitriol chamber may be regarded as the direct addition of oxygen to nitric oxide, forming nitrous anhydride, and the reaction of this with sulphur dioxide and steam to form sulphuric acid reproducing nitric oxide, thus furnishing a cycle of great simplicity.

$$(3)\ 4NO + O_2 = 2N_2O_3.$$
$$(4)\ SO_2 + N_2O_3 + H_2O = H_2SO_4 + 2NO.$$

The action is thus viewed as consisting in the reaction on one another of *gaseous* substances only—viz. steam, oxides of nitrogen, and sulphur dioxide, with the result of yielding a product not gaseous at the prevailing temperature—viz. sulphuric acid; the latter consequently precipitates in the liquid state in the form of fine mist or suspended vesicles, which forthwith attract more water from the atmospheric vapour present, thus becoming vesicles of diluted sulphuric acid. If sufficient water vapour be not present to enable reaction (4) to take place, instead of *liquid* vesicles of diluted sulphuric acid being formed, a kind of snow or hoarfrost deposits in the *solid* state, consisting of nitrosyl sulphuric acid[1] (otherwise known as nitrosyl sulphate, nitrosulphonic acid, nitro-sulphuric acid, or from its mode of formation 'chamber crystals') produced in virtue of the reaction

$$(5)\ 2SO_2 + 3N_2O_3 + H_2O = 2SO_2(OH)(NO_2) + 4NO.$$

In any case this substance may be supposed to be formed as a temporary intermediate product, being decomposed instantly in presence of excess of steam in accordance with the reaction

$$(6)\ 2SO_2(OH)(NO_2) + H_2O = 2SO_4H_2 + N_2O_3.$$

So that the complete cycle may be regarded as really consisting of reactions (3) and (5) continually forming nitrosulphonic acid, which then becomes sulphuric acid in virtue of reaction (6), no oxide of nitrogen higher than N_2O_3 being involved at all in the changes.

Another way of explaining the changes, still representing nitric oxide as the main carrier, is to regard that gas as taking up oxygen to form N_2O_4 which then reacts like N_2O_3 in the previous equations, giving the simple cycle—

$$(7)\ 2NO + O_2 = N_2O_4$$
$$(8)\ 2SO_2 + N_2O_4 + 2H_2O = 2H_2SO_4 + 2NO.$$

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[1] In Ward's rough process of 140 years ago, 8 parts of sulphur were employed to 1 of saltpetre; or 12·5 parts of potassium nitrate, equivalent to 10·5 of sodium nitrate, per 100 of sulphur.

[1] *Nitrosulphonic acid*, strictly speaking, implies the atomic arrangement $SO_2{<}^{OH}_{NO_2}$, where the nitrogen of the NO_2 group is directly linked to the sulphur of the SO_2 group. *Nitrosyl sulphuric acid*, on the other hand, implies the arrangement $SO_2{<}^{OH}_{O-NO}$, where the nitrogen is only indirectly linked to the sulphur by the agency of oxygen.

Or, admitting the formation of nitrosulphonic acid as an intermediate product, as giving the cycle furnished by reaction (7) followed by

(9) $4SO_2 + 3N_2O_4 + 2H_2O = 4SO_2(OH)(NO_2) + 2NO$

the nitrosulphonic acid being either split up by excess of steam in accordance with equation (6), or thus[1]

$$(10)\ 4SO_2(OH)(NO_2) + 2H_2O$$
$$= 4H_2SO_4 + N_2O_4 + 2NO.$$

A modification of this view supposes that nitrosulphonic acid is formed by the reaction

$$(11)\ 2SO_2 + 2N_2O_4 + H_2O$$
$$= 2SO_2(OH)(NO_2) + N_2O_3$$

the N_2O_3 thus formed giving more nitrosulphonic acid in accordance with reaction (5), equation (9) being thus equivalent to the sum of (11) and (5); whilst another modification supposes that both N_2O_3 and N_2O_4 are directly formed from NO by reactions (3) and (7), and then give rise to nitrosulphonic acid by reactions (5) and (9), which then finally gives sulphuric acid by the reaction of excess of steam as before. Perhaps of all the foregoing views, this last one has been most widely adopted.

In connection with all theories regarding N_2O_4 as playing an important part in the cycle of changes, Lunge and Naef have shown (S. C. I. 1884, 633) that no measurable quantity of nitrogen tetroxide can be detected in the atmosphere of a chamber working normally (although it may appear in the last chamber when practically all sulphur dioxide has disappeared); so that if reaction (7) takes place at all during ordinary working, the N_2O_4 formed has only a transitory existence (like nitrosulphonic acid in presence of excess of steam), being instantaneously reduced again by the sulphur dioxide.

Yet other explanations of the chamber process have been given by different chemists, nitric oxide being still regarded as the main carrier; one of the most recent of these is that advocated by Raschig (B. 1887, 1161), who supposes that nitric oxide, steam, and oxygen unite together to form orthonitrous acid, $N(OH)_3$, which then combines directly with sulphur dioxide, forming a hypothetical body, dihydroxylamine sulphonic acid; this substance has only a momentary existence, being forthwith acted on further by orthonitrous acid, producing diluted sulphuric acid and nitric oxide, which recommences the cycle;[2] thus—

$$(12)\ 4NO + O_2 + 6H_2O = 4N(OH)_3$$
$$(13)\ N(OH)_3 + SO_2 = N(OH)_2.SO_2(OH)$$
$$(14)\ N(OH)_2.SO_2(OH) + N(OH)_3$$
$$= SO_2(OH)_2 + 2H_2O + 2NO.$$

All these views have two points in common: firstly, they regard the reactions as taking place between substances *in the vaporous* [illegible] in the first instance; and secondly, they regard *nitric oxide* NO *as the essential carrier.* As regards the first point the author has long regarded it as more probable that the main portion of the normal action of a vitriol chamber *does not go on in virtue of the inter-reaction on one another of gaseous or vaporous substances solely, but takes place on the surface of the liquid water vesicles formed by the partial condensation of the steam at the moment of its entering the chamber.* If acid of 120°Tw. is made, approximately $2SO_3,7H_2O$, for every volume of sulphur dioxide used about 3·5 volumes of water vapour are requisite to form such acid. Hence 100 vols. of burner gases containing 8 to 9 vols. of SO_2 would correspond with 28 to 32 vols. of water vapour; but gases saturated with aqueous vapour at 50° (tension = 92 mm.) could only contain some 12–13 p.c. by volume of aqueous vapour, or less than half that requisite to form vitriol of 120°, even if the presence of sulphuric acid in a large fraction of the vesicles floating about did not diminish the tension of aqueous vapour below 92 mm., and so prevent so large an amount being retained in the vaporous state. According to Sorel's experiments (p. 710), the tension of aqueous vapour in contact with acid of 120°Tw. is only 7 mm. at 50°C., so that the gases would, under these conditions, only contain about 1 p.c. of aqueous vapour. Hence *the greater part of the steam blown in* (reckoning that from the Glover tower as well) *must precipitate as vesicles of liquid water mist immediately on entering the chamber.*[1] The gases thus are in contact with a large surface of floating liquid water particles; without begging the question as to what are the precise chemical reactions going on, it is at least obvious that the surface-action of this liquid water must cause a large part of the chemical changes to take place thereat, and that the final result must be to convert each water vesicle into one containing dissolved sulphuric acid, the action going on until the acid solution becomes of considerable strength and attracts moisture to itself from the vapour in the chamber atmosphere, thus increasing in weight continually, and finally either falling to the bottom under the influence of gravity, or being carried by the air currents against the walls like fine rain. Obviously, when 'pulverised' water and not steam is supplied to the chamber, *the chemical action must of necessity take place on the surface of the water particles.* A noteworthy consequence as regards the disappearance of 'available' oxides of nitrogen in the chamber, discussed at more length below (p. 729), results from this supposition that the chemical changes largely go on *at the surface of the floating vesicles*, and necessarily therefore in the first instance *between gases in contact with pure water or highly dilute acid.*

As regards the second point, a theory of the vitriol chamber process has been put forth by Lunge (C. J. Trans. 1885, 470; also B. 1888, pp. 67 and 3223), which supposes that *nitrous anhydride* N_2O_3, [illegible] is the main carrying agent, the latter oxide not existing at all in the chamber gases excepting in so far as it is formed in the earlier portion of a series of chambers by a comparatively secondary reaction. Lunge re-

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[1] In contact with excess of *pure water*, chamber [illegible] form sulphuric acid together with [illegible] and nitric acid, either in accordance [illegible] the nitroso-nitric anhydride thus [illegible] acted upon thus $N_2O_4 + H_2O = HNO_2 + HN$[illegible] virtue of reaction (6), the nitr[illegible] acted upon by water, thus:

$$N_2O_3 + H_2O = 2NO_2H$$
$$3NO_2H = NO_3H + 2NO + H_2O.$$

[2] For further [illegible] Raschig's [illegible] Lunge's criticisms thereon, v. Lunge, B. 1888, 67 and 3223; Raschig, A. 248, 123; Hamburger, S. C. I. 1889, 164.

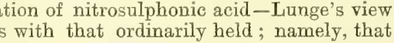
[1] According to Lunge's calculations, at least three-fourths of the entering steam is at once condensed to liquid water particles, even if the diminished tension through contact with acid be not taken into account.

gards the main cycle action as being, firstly, a condensation of nitrous anhydride, sulphur dioxide, aqueous vapour, and oxygen to form liquid vesicles of nitrosulphonic acid; thus

(15) $2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)(NO_2)$;

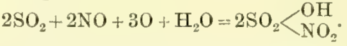
and secondly, the reaction on these of liquid water (or highly dilute sulphuric acid) vesicles (floating about as a mist in the chamber atmosphere like the nitrosulphonic acid itself), forming sulphuric acid and reproducing nitrous anhydride in accordance with equation (6). Any arrangement which facilitates the coming in contact of the two kinds of vesicles, so as to react mutually on one another, consequently renders the production of vitriol more rapid. So far as the first part of the change is concerned—namely, the formation of nitrosulphonic acid—Lunge's view agrees with that ordinarily held; namely, that the reaction consists in the mutual combination or other action on one another of *substances in the gaseous or vaporous condition* to form liquid nitrosulphonic acid vesicles (subsequently further acted upon by water vesicles); and differs from the author's view that, although reaction between gaseous substances may and no doubt does take place, still the larger part of the changes are effected *on the surface of the liquid water vesicles* produced by the condensation of steam or supplied as 'pulverised' water, thereby gradually converting these into vesicles of dilute sulphuric acid.

Besides the leading and fundamental cycle of reactions above mentioned, Lunge regards several secondary changes as taking place; thus in the first chamber of a system a reaction occurs whereby a portion of the nitrosulphonic acid is denitrated by sulphurous acid, forming nitric oxide:

(16) 

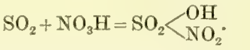
$$2SO_2{<}^{OH}_{NO_2} + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

The nitric oxide thus formed reacts with oxygen, sulphurous acid, and steam to reproduce nitrosulphonic acid:

(17) 

$$2SO_2 + 2NO + 3O + H_2O = 2SO_2{<}^{OH}_{NO_2}.$$

If any nitric acid be present, either formed in the chamber or directly introduced into it as such, it is converted into nitrosulphonic acid:

(18) 

$$SO_2 + NO_3H = SO_2{<}^{OH}_{NO_2}.$$

If any nitrogen tetroxide be formed, it becomes reduced to nitric oxide with formation of sulphuric acid, in accordance with equation (8). Some part of the nitrous acid similarly acts directly on sulphurous acid, becoming reduced to nitric oxide and forming sulphuric acid, in accordance with equation (4).

E. Sorel (Bull. Soc. Ind. Mulhouse, 1889, 240; also S. C. I. 1890, 175), in an elaborate memoir on the manufacture of sulphuric acid, has put forth a theory very similar to Lunge's as regards the nature of the leading actions taking place—viz. formation of nitrosulphonic acid from nitrous anhydride, sulphur dioxide, oxygen, and water vapour, and its subsequent decomposition under the influence of more water vapour into sulphuric acid and nitrous anhydride; he also admits, however, that various other subsidiary reactions take place, involving NO and N_2O_4, and considers that the successive oxidations and reductions of the oxides of nitrogen which determine the transformation of sulphurous acid to sulphuric acid are brought about by variations in the degree of hydration of the sulphuric acid suspended in the gases, and that in the apparatus ordinarily used these variations of hydration *are brought about by changes of temperature*, and are in direct relation to these; whence he concludes that the working of a sulphuric acid apparatus can be advantageously modified by increasing artificially and at certain points the concentration of the acid in contact with the gases, and denitrating this acid at opposite points, so as to bring about an active circulation of the oxides of nitrogen between the neighbouring zones.

Whichever of these various views as to the nature of the chemical reactions taking place be regarded as most probable (about which opinions still differ considerably, although Lunge's views are now accepted by many), no doubt whatever can be entertained that none of them accounts for the whole of the chamber phenomena; more especially for the circumstance that even with the best designed and most perfectly working system of nitrous fume recovery, a continuous consumption of nitre is indispensable to the working of the process far exceeding the amount of available nitrogen oxides lost by defective absorption in the Gay-Lussac tower, by conversion into insoluble nitric oxide, and by leakage and solution in the chamber acid. From 3 to 4 parts of nitre continually consumed per 100 of sulphur burnt as pyrites is a very usual proportion, although in some cases smaller amounts (sometimes even below 2 parts, for a time at any rate) are required; of this *at least* from 1·5 to 2·5 parts *entirely disappear* so far as their existence is concerned in forms capable of taking part in the cycle of vitriol-forming changes—*i.e.* they become converted into nitrous oxide, N_2O, or even into free nitrogen. Considerable difference of opinion has prevailed as to the actual proportion of nitre lost in well-conducted works in the form of available nitrogen oxides escaping condensation in the Gay-Lussac tower, partly as NO, partly as higher oxides; thus, figures have been obtained by Lunge, Davis, Jackson, Mactear, and others indicating amounts of escape equivalent to from 1 to 1·75 parts of nitre per 100 of sulphur burnt as usual proportions; whilst Hurter, Eschellman, and others consider ·25 to ·5 as more nearly the amount thus lost on the average with efficient plant in good working order. From the results obtained in a variety of works Hurter concluded (C. N. 39, 170) that the total loss of nitre from 'mechanical' sources (*i.e.* defective absorption of higher oxides, formation of nitric oxide, leakages, and solution in chamber acid jointly) does not amount to as much as 25 p.c. of the nitre potted, at least 75 p.c. being lost by chemical secondary changes. E. K. Muspratt states (S. C. I. 1884, 137) that the result of experiments made in ten different works by a committee of the Alkali Makers' Association was that the total loss by non-absorption in the Gay-Lussac tower averaged close to 20 p.c. of the nitre used, that being 4 parts per 100 of sulphur burnt. Eschellman found (S. C. I. 1884, 134) that out of 2·75 parts of nitre per 100 of sulphur burnt, 0·33 parts = 12 p.c. was accounted for by the non-absorption in the Gay-Lussac tower of soluble nitrogen oxides,[1] and 0·19 part more = 7 p.c. by the formation of nitric oxide, representing a total of ·52 parts = 19 p.c. of loss due to available nitrogen oxides of all kinds; to which ·08 parts = 3 p.c. must be added as the amount of nitre equivalent to leakages and retention in the denitrated vitriol; thus leaving 2·15 parts = 78 p.c. not accounted for by 'mechanical' losses, but destroyed by secondary chemical changes.

As regards the way in which these changes are brought about, and the part of the plant in which they mainly take place, very divergent opinions have been held; for a long time the Glover tower was blamed, it being supposed that the nitrous vitriol run through the tower was acted upon by the sulphur dioxide of the burner gases so as largely to reduce the higher oxides to N_2O; but this idea has been practically exploded, because the bulk of the denitration in the Glover tower takes place in the upper portion where the temperature is not high enough to enable sulphur dioxide to exert any marked action of the kind in the presence of acid of the strength of that passing through the tower (about 200°C. being requisite according to Lunge, or far above the temperature of the top of the tower); further, just as good results are obtained when nitric acid is run through the tower as when it passes into the chambers by 'cascade,' which could not be the case if any considerable destruction of nitrogen oxides took place in the tower; whilst the quantity of available nitrogen oxides contained in the gases passing out of the tower can be shown analytically to correspond practically with the quantity contained in the nitrous vitriol run into the tower. These facts equally dispose of the belief held by some that the loss is due to the reducing reaction of the arsenious oxide contained in pyrites acid upon the nitrogen oxides contained in the vitriol sent through the Glover tower; moreover, in the manufacture of brimstone acid where no arsenic is present, the same disappearance of available nitrogen oxides takes place. The Gay-Lussac tower has been considered by others to be the seat of the disappearance, either by the reaction of arsenious oxide, the reducing action of the coke packing, or through some other similar cause; but this view again is disproved by the occurrence of the loss with brimstone acid, and by the circumstance that under ordinary conditions practically all available nitrogen oxides entering the tower can be analytically accounted for, either in solution in the emerging vitriol, or in the escaping gases. Hence it results that the disappearance of available nitrogen oxides must take place *mainly in the chambers themselves*, in virtue of secondary reactions; but the precise way in which these are brought about has always been a matter of uncertainty.

It has long been known from the experiments of Pelouze and Weber, more recently repeated and amplified by Lunge, that in contact with water or highly dilute sulphuric acid higher oxides of nitrogen are slowly acted upon by sulphur dioxide, with the formation of nitrous oxide, thus

$$N_2O_4 + 3SO_2 + 3H_2O = N_2O + 3H_2SO_4$$
$$N_2O_3 + 2SO_2 + 2H_2O = N_2O + 2H_2SO_4$$
$$2NO + SO_2 + H_2O = N_2O + H_2SO_4$$

but in contact with stronger acid these actions take place either not at all, or only extremely slowly; so that it does not appear likely that the conditions ordinarily regarded as obtaining in the chambers would be such as to enable these changes to go on to any considerable extent, except in the immediate vicinity of the entering steam, where the aqueous vapour would locally be in sufficiently large excess. The author's view of the physical character of the chamber reactions above alluded to (viz. that *the bulk of the action takes place, not between gases as such, but between gases in contact with the surface of liquid water vesicles produced by the condensation of steam*), however, readily accounts for the impossibility of avoiding nitre-destruction in the chambers, because on that supposition the reacting gases must of necessity at first find themselves in presence of a relatively large excess of water, the vesicles first condensed being practically pure water, and only becoming comparatively strong acid after some considerable time, during which period all the conditions are present requisite for the formation of nitrous oxide by the reducing action of sulphur dioxide only. Moreover, the higher nitrogen oxides present are perpetually in a *quasi-nascent* state in virtue of their carrier action; so that the reducing effect of sulphur dioxide would naturally be more marked than in the case of free nitric oxide &c. not nascent. In order to effect the transformation of a large quantity of sulphur dioxide into vitriol by means of a small quantity of nitrogen oxide, the cycle of changes (whatever it may happen to be) must be repeated a large number of times, as is shown by the following considerations. If the chief reactions occurring are those represented by equations (7) and (8), one atom of sulphur (as dioxide) is converted into sulphuric acid for one of nitrogen combined as oxide at each repetition of the cycle; but with a nitre consumption of, say, 3·5 parts of sodium nitrate per 100 of sulphur burnt, the number of nitrogen atoms relatively to the sulphur atoms present in the chamber gases is approximately only as 1 to 75; for 100 parts of sulphur would correspond with $\frac{85}{32} \times 100 = 265{\cdot}6$ parts of nitre, and $\frac{265{\cdot}6}{3{\cdot}5} = 75$ nearly; so that in this case the cycle must be repeated some 75 times in order to convert all sulphur dioxide into sulphuric acid. The same result follows if Lunge's theory of the

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[1] The following figures were obtained [illegible] the average daily tests for periods of [illegible] different sets of chambers were [illegible] oxide of nitrogen being [illegible] actual nitre employed.

Set of chambers	Cubic metres [illegible] sulphur burnt	Nitre per [illegible]	[illegible]	[illegible] by acid [illegible]
No. 1 . . .	1·34	[illegible]	[illegible]	10·7
No. 2 . . .	1·34	[illegible]	[illegible]	12·2
No. 1 . . .	[illegible]	2·75	[illegible]	11·5
No. 2 . . .	1·17	2·55	7·0	12·5
		Mean . . .		[illegible]

chamber reactions be adopted. On the other hand, if the essential changes be supposed to be those indicated by equations (3) and (4), one atom of sulphur (as dioxide) is converted into sulphuric acid for *two* of nitrogen present as dioxide at each repetition of the cycle; whence the cycle must be repeated twice as often, say 150 times, in order to convert all sulphur dioxide into sulphuric acid. These figures, 75 and 150 times respectively, are, of course, subject to considerable modification—on the one hand, because the quantity of available nitrogen oxide is continually decreasing, owing to conversion into inert bodies; on the other, because the regenerative action of the Gay-Lussac tower causes more nitrogen oxides to be actually present in the chambers at any given moment than corresponds with the nitre actually consumed;[1] but the calculations are sufficiently exact to show that if it be granted that a trace of nitrous oxide (or possibly of free nitrogen) is produced at each repetition of the cycle in virtue of the reducing action of sulphur dioxide on quasi-nascent higher oxides of nitrogen in contact with a surface of liquid water or dilute sulphuric acid, the total destruction of higher oxides ultimately brought about may amount to something very considerable.

If this view be correct, it should result that if the total surface of water particles in operation be increased by blowing in more steam, a more rapid rate of destruction of available nitrogen oxides should be brought about. In point of fact, this is the case.[2] Thus Eschellmann (S. C. I. 1884, 134) found that increasing the amount of steam admitted to four equivalents, instead of three, relatively to the acid made, caused an additional destruction of available nitrogen oxides requiring an increment in nitre-consumption to balance it of 10·5 p.c. (2·75 parts nitre per 100 of sulphur burnt being the original consumption). Similarly, when chambers are worked without Gay-Lussac towers and weak vitriol is made in the last one by blowing in a large amount of steam, a very large destruction is brought about. In various observations made by the author the quantity of available nitrogen oxides thus destroyed throughout the entire series of chambers represented *more than half* of the nitre consumed; *i.e.* when 10 parts of nitre per 100 of sulphur burnt were employed, the available oxides of nitrogen escaping in the exit gases and condensed in the total vitriol made never jointly averaged an amount equivalent to as much as 5 parts of nitre. Again, it is well known that, on freshly starting a chamber, if water or very weak acid be used to cover the floor, a large destruction of available oxides always takes place until the bottom acid becomes strong enough to prevent the reducing action of the sulphur dioxide being facilitated by the large surface of watery liquid thus exposed.

Apparatus for supplying nitrogen oxides. In the early days of vitriol-making, *saltpetre*—*i.e.* potassium nitrate—was the only salt practically available; but this has so long been superseded by the cheaper 'Chili saltpetre' or 'soda nitre' (approximately pure sodium nitrate[1]) that the term *nitre* in the vitriol trade is practically always understood as referring to the latter. From this as prime source four distinct methods of impregnating burner gases with nitrous fumes are, or have been, employed—one consisting in distilling off nitric acid therefrom by the action of sulphuric acid in separate retorts (*v.* NITRIC ACID), and then bringing the liquid acid in thin films (produced by trickling over earthenware 'cascades,' *&c.*) in contact with the hot burner gases, whereby nitrogen oxides are rapidly produced in virtue of the reactions above-mentioned; or introducing it into the Glover tower along with the nitrous vitriol; the second in effecting the same result by evolving the nitric acid in the state of vapour, in moderately small quantities at a time, by introducing into the hot burner flue pots containing a few pounds of nitre mixed with sulphuric acid, so that the nitric acid vapours are acted upon as above whilst almost nascent; the third in oxidising molasses or metals and such-like substances with separately prepared nitric acid, leading off the fumes of oxides of nitrogen to the chambers, and utilising the resulting oxalic acid &c. for sale; and the fourth in continuously introducing the nitre dissolved in water (and sometimes acidulated with sulphuric acid) either into the chamber in the form of spray, or into the Glover tower. Of these, the first and second plans are still widely adopted; the third has practically fallen into disuse, although still employed occasionally on a small scale to utilise waste nitrous fumes arising from other processes involving oxidation by nitric acid; and the fourth is seldom or never used now, partly because the acid so produced necessarily contains sodium sulphate (not an important impurity for some purposes—*e.g.* the Leblanc alkali process and the manufacture of saltcake); but chiefly because extra wear is usually occasioned when the liquid is injected into the chambers, whilst stoppage from crystallisation of solid sodium sulphate is apt to occur when it is used in the Glover tower.

The use of liquid nitric acid separately prepared has the advantage of enabling a more equable and steady development of nitrous fumes to be produced than is practicable by the use of 'nitre-pots,' whilst it also avoids the admission of air into the flues, which unavoidably takes place during discharging and re-charging the pots; further, should, for any reason, an extra supply of nitrous fumes be temporarily requisite, this can be instantly procured by increasing the rate of flow of the acid. On the other hand,

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[1] Usually from 10 to 20 parts of nitre in circulation per 100 of sulphur burnt, as compared with 2 or 3 actually destroyed; with 'forced working' (p. 737) still larger amounts of active nitrogen oxides are in circulation.

[2] This result is not incompatible with the more rapid rate of formation of liquid vitriol by transformation of sulphur dioxide, effected by increasing the steam supply under suitable conditions (*v.* p. 734); nor with the accelerating effect of the 'plate column,' due to the increased amount of contact between the gases and films of watery fluid thereby brought about (p. 748).

[1] The average composition of nitrate of soda as used for vitriol making may be taken to be:

Sodium chloride	0·5	
Sodium sulphate	0·75	
Moisture	2·75	
Total 'refraction' (impurities) . . .		4·00
Nitrate of soda (by difference) . . .		96·00
		100·00

When the chloride present exceeds 1 p.c., the substance is apt to cause a considerable amount of loss of nitrogen oxides in the chambers.

it involves extra cost in distilling off the acid, and more outlay for labour, carboys, and appliances for supplying the acid to the gases; and, in case of accidents, it is liable to cause corrosion of the chambers when not introduced through a Glover tower. Some makers also are under the impression that rather more nitre is requisite when used in this way than when employed in pots; although others find that this is not the case. Opinions differ accordingly as to the relative advantages of the two processes, many Continental manufacturers considering that the advantages of the liquid acid method preponderate, whilst the majority of British vitriol-makers are of the opposite opinion, especially when the modification of the potting process described below is used, which obviates several of the chief objections to that process in its simplest form.

When the liquid acid method is employed, the acid is usually brought into contact with the gases, not in the flue leading to the chambers, but in the chamber itself (usually a smaller preparatory one), being made to run intermittently or regularly in a stream over some distributing arrangement exposing a large surface; such as a tall pyramid of dishes and cylinders, a series of shorter pyramids, a set of large flat dishes or trays at different levels, each overflowing into the next, or an earthenware cascade and dish combination. In this way the volatilisation of the whole of the acid is effected before it reaches the lowest dish &c., to which, however, it is well to affix an overflow pipe outside the chamber to prevent corrosion in case of an unduly large supply of acid causing running over. When an intermittent supply is used it is conveniently obtained by the well-known 'tumbling box,' fed regularly by a Mariotte's bottle, so as to obtain a constant rate of delivery as long as the acid level in the bottle does not fall below the line corresponding with the lower extremity of the air-pipe; or a miniature flushing tank may be used instead of a tumbling box. Another method of introducing the acid into the chambers consists of 'pulverising' it by a spray jet, analogous to that used for water-supply by Sprengel (p. 733). Various forms of apparatus for this purpose have been constructed. A much simpler method, however, is to feed the acid in along with the nitrous vitriol and chamber acid at the top of the Glover tower, whereby all danger of corrosion through overflowing &c. is avoided without introducing any corresponding inconvenience; for although at one time it was thought that this mode of supply was likely to cause loss through too great decomposition by overheating, nitrous oxide or nitrogen being supposed in that case to be formed, experience has not borne out this idea, no increase in the consumption of nitre requisite having been noticed in various cases when this method of supply was substituted for the cascade system (Lunge).

The nitre-pot system, when applied to brimstone burners of the simplest kind (p. 23), is carried into effect by placing a cast-iron 'pot,' holding the mixture of nitre and sulphuric acid, on the floor of the burner so as to become heated by the burning sulphur. Should the contents of the pot froth over, as often happens, sulphur is thus wasted and damage done. Preferably, therefore, the pot is not placed actually in contact with the burning brimstone, but beyond it, so as to be heated by the flame and current of hot gases as in Blair's burner (p. 723). In this position, however, it may happen with small-sized burners that the heat is not sufficient to work off the pot in the proper time. When nitre pots are similarly used with pyrites burners, if so situated that boilings over can run into the burner, fritting together of the lumps is likely to ensue; wherefore, it is usual to place all the pots together in a 'nitre oven' (*i.e.* an enlargement of the flue, with a door in front for introducing and withdrawing the pots by means of a stout fork), situated just beyond the last kiln in the range so as to be as much heated as possible. To prevent damage to brickwork, a cast-iron tray is generally provided at the bottom of the oven to catch boilings over. In order to keep up as equable a supply of nitrous vapours as possible, the pots are not all charged and discharged at once, but alternately in batches at regular intervals, so that some are fresh and evolve acid vapours freely, whilst others are partly worked off, and others approaching exhaustion; or, better still, two or more separate ovens are used, the contents of which are thus alternately recharged.

W. Crowder finds that the frequent breakages occurring from the sudden chilling of hot nitre-pots on introducing a fresh charge are best avoided by fixing the pots *outside* the flue, heating them with a small coke fire, and not by the burner gases (S. C. I. 1891, 295). Moreover, the heat can be much more exactly regulated in this way.

Owing to the large volume of air which necessarily enters the flues when the oven doors are opened, and the simultaneous loss of gases by passage outwards, an arrangement has latterly come into use whereby this opening of the doors is avoided. The pot is provided with a tubular spout at one end, which is plugged up when in use, and projects outwards from the oven. When the charge is spent the fused 'nitre-cake' (acid sodium sulphate—often designated 'Sally Nixon,' *i.e. sal enixum*) is withdrawn by taking out the plug, when the liquid mass runs out into a suitable receptacle. The plug is then replaced, and a fresh charge passed into the pot by means of a small hopper or funnel in the top of the oven, the nitre being first introduced, and then the sulphuric acid, after which the hopper is plugged up gas-tight. As with this arrangement the pot does not require to be lifted out by means of a fork for discharging, it can be made much bigger so as to hold a larger charge. Thus, whilst from 7 to 14 lbs. of nitre at a time are usually worked off in the ordinary movable pots, ½ cwt. charges can be used in the stationary pot. To equalise the evolution of nitrous fumes, two or more stationary pots, charged alternately at equal intervals of time, are worked together.

6. **Supply of aqueous vapour.** When no Gay-Lussac and Glover towers are used, all the water ultimately transformed into chamber acid must be supplied in the form of steam, the small amount of aqueous vapour present in the air used for combustion being at least balanced by that carried off in the spent gases. In this case, assuming the chamber acid to have an average strength of 120 Tw. (representing the composi-

tion 68·7 p.c. H_2SO_4, and 31·3 p.c. additional water), it is obvious that $\frac{32}{98} \times 68{\cdot}7 = 22{\cdot}4$ parts of sulphur are present relatively to $\frac{18}{98} \times 68{\cdot}7 + 31{\cdot}3 = 43{\cdot}9$ parts of water, including that combined as sulphuric acid; *i.e.* the total steam to be admitted must be $\frac{43{\cdot}9}{22{\cdot}4} = 1{\cdot}96$ times, or almost exactly double the sulphur burnt. If, however, both Gay-Lussac and Glover towers be used, and all the acid made be passed through the latter, supposing the resulting evaporated acid to have an average strength of 145°Tw. (corresponding with 79·25 p.c. H_2SO_4 and 20·75 p.c. additional water), much less steam will obviously be required; neglecting the aqueous vapour contained in the air (that carried out by the spent gases being only inconsiderable, the Gay-Lussac tower drying them pretty thoroughly), the acid contains now $\frac{32}{98} \times 79{\cdot}25 = 25{\cdot}9$ parts of sulphur relatively to $\frac{18}{98} \times 79{\cdot}25 + 20{\cdot}75 = 35{\cdot}3$ parts of water; whence the steam requisite will be $\frac{35{\cdot}3}{25{\cdot}9} = 1{\cdot}44$ times the sulphur burnt. Analogous calculations apply in the case of other degrees of concentration; as the above strengths are not far removed from the usual working averages, it may fairly be inferred that when Glover towers are used, the steam required will not be far from $1\frac{1}{2}$ times the sulphur burnt; and when they are not used, close to double the sulphur burnt, or more if the acid has a low average strength. A somewhat larger amount of boiler evaporation will, however, be required, as a not inconsiderable amount of the steam unavoidably condenses in the supply pipes; these should, of course, be swathed as much as possible with non-conducting coatings to diminish condensation.

Some considerable time ago it was not unusual to mount boilers for supplying steam over the burners so as to utilise the heat of combustion of the pyrites; but various difficulties in the way of obtaining sufficient heat and uniformity of pressure have caused this to be generally given up in favour of separately fixed boilers burning coal, the heat from the pyrites burners being preferably utilised in the Glover tower, or by heating lead pans for the evaporation of chamber acid. Steam of high pressure is in no way necessary to carry a jet well through a chamber, one atmosphere of excess pressure being usually quite sufficient to traverse the whole length, unless when of very exaggerated dimensions; but the higher temperature of high pressure steam diminishes the inconvenience of condensation in the steam mains, and in winter helps to overcome the chilling effect of an excessively cold external atmosphere; so that whilst in Britain 1 to $1\frac{1}{2}$ atmospheres pressure is a usual working limit, in France 2 to 3 atmospheres is employed with good results in cold weather (Lunge and Naville). Fig. 4 represents a steam jet, the tube CC passing into the chamber through the wall EE by a stuffing-box DD, B being the regulating cock, A the connection with the steam main, and F G a mercurial gauge affixed by means of the ┳ joint H so as to indicate the pressure of the entering steam. Uniformity of pressure to insure uniformity of steam supply is practically of much more importance than the absolute value of boiler pressure; to insure this, automatic regulators are employed in some works, the effect of which is to give a uniform pressure in the steam main, no matter what may be the boiler pressure, provided the latter does not fall below a particular limit. Usually, several boilers are worked together into the same main so that variations of pressure in one make comparatively little difference in the total supply. Sometimes an automatic diagrammatic pencilling arrangement is employed, giving a tracing indicating at a glance any variations in pressure that have taken place.

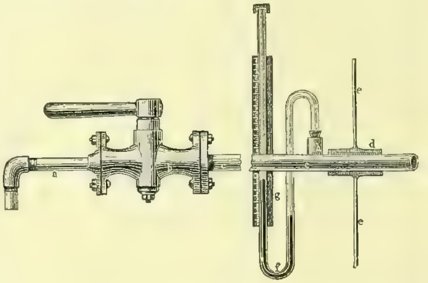

FIG. 4.

Practice differs considerably in different countries and amongst different manufacturers as to the method adopted for the introduction of steam so as to mix uniformly with the burner gases. Only a fraction of the steam admitted remains permanently in the vaporous state, the majority condensing instantly to vesicles of mist, which float about in the gases (p. 727); as above stated, the reaction between the gases probably mainly takes place on the surface of these liquid water vesicles, gradually converting them into vesicles of more or less dilute sulphuric acid. In some works a number of different jets are preferred, playing into the same chamber, either downwards through the roof, or sideways through the walls, at equidistant intervals; in others, one only is introduced, either close to the orifice of the tube through which the burner gases enter, or concentrically within it, so that the aspirating action of the steam jet aids the draught—this form is especially in favour in Great Britain. Jets passing upwards through the floor have been employed, but are open to grave objections, as sooner or later a leak, difficult of access, is inevitably produced in the base or 'saucer' of the chamber. Jets introduced at the far end in opposition to the general direction in which the gases flow are sometimes employed, but, of course, tend rather to impede the draught.

In 1873 Sprengel patented the employment of 'pulverised' water—*i.e.* water reduced to a mist-like spray by blowing a jet of steam at about two atmospheres pressure through the inner of two concentric tubes (fig. 5), through the larger outer annulus of which the water is made to flow from a tank at a higher elevation.

With a properly proportioned compound jet 4 parts by weight of water can be converted into fine spray by 1 of steam; but with incorrect proportions larger drops are apt to be formed which do not remain suspended long enough to produce the proper effect, and consequently fall and dilute the acid at the bottom. The spray does not carry as far as a steam jet, wherefore in a large chamber several jets are requisite placed in the sides about 40 feet apart. The advantages claimed for the use of spray instead of steam are that not only is fuel saved, less actual steam being required, but also that the mean temperature of the chamber is lowered, so that it holds a greater weight of gases, which is virtually the same thing as an increment in dimensions without additional cost. The disadvantages were thus summed up by G. Lunge (Manufacture of Sulphuric Acid and Alkali, 1st edit. vol. i. p. 327): 'The spray jet contributes next to nothing to the draught, and very little to the mixing of the gases, as the steam jets mix them; and the cooling of the chamber is easily carried too far below the temperature of 54°C. or even 40°C. (*the minimum*), usually assumed as the most favourable for the process. Nor can it be assumed that a large chamber can in this way be so uniformly supplied with moisture as by a steam jet; and only in the first and hottest part of the jet might the spray jet be employed with some advantage. In order to feed a chamber by spray jets it would have to receive a number of apparatus; and the complication of work caused thereby, as well as the other drawbacks mentioned above, will not be counterbalanced by the saving of coals, which will hardly be very considerable. In fact, it does not appear that Sprengel's apparatus has made much way amongst alkali works.' On the other hand, Lunge has stated that pulverised water (produced by the mechanical action of a fine stream issuing under a pressure of 2 atmospheres from a platinum nozzle on to a platinum button) has been successfully applied at Griesheim, where fuel is dear, the saving of fuel more than compensating for any inconveniences, more especially in this case for the cost of filtration, which is indispensable to avoid blocking up of the fine jets used. Two rows of water jets are introduced through tubes in the chamber tops, each tube about 20 feet apart from the others. Thus the whole chamber is uniformly filled with a fine mist, which, together with the steam coming from the Glover tower, supplies all the water required for the chamber process. Later experiments by Lunge and Naef (Chem. Industrie, 1884, 5) have led them to believe that the cooling effect of Sprengel spray jets is but small as compared with the heat developed by the chemical processes, and with the effect of variations in the temperature of the external atmosphere. Thus the same set of chambers, furnished with a number of thermometers at different points, gave readings on two days (on which the external air was at 12° and 24° respectively, steam being used on the first day and spray on the second) indicating that whilst the difference between the external air and each point was somewhat less on the second day than on the first, yet the absolute temperatures at each point were higher on the second day, the cooling effect of the spray jet being more than compensated for by the higher atmospheric temperature retarding cooling by convection and radiation. Again, the gases from the Glover tower at Griesheim, having a temperature of about 35°C., are quickly raised in the first chamber to 50° by the chemical action, notwithstanding that no steam is introduced. At Freiberg, burner gases are often cooled to 0° in winter to condense arsenic; but on entering the chamber the temperature soon rises to upwards of 50°.

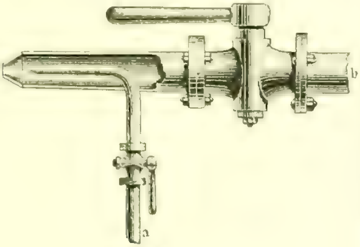

Fig. 5.

A later patent has been taken out by Sprengel (10,798, Aug. 1886) for utilising exhaust steam from engines for vitriol-making, the boilers being worked at about 10 lb. pressure more than would otherwise be necessary, and the engine being so arranged that the exhaust steam leaves it at a pressure of about 10 lbs., sufficient to work the chamber-jets.

7. Chambers: conditions regulating dimensions. The processes going on in the chambers are, as above stated, of such a character that a variety of views are current amongst different chemists as regards their actual nature and the exact chemical reactions taking place. The end result, however, so far as the conversion of sulphur dioxide, oxygen, and steam into vitriol is concerned, is one admitting not only of no misinterpretation, but of the application thereto of mathematical calculation with a considerable degree of concordance between the calculated results and those observed in practice whenever sufficiently precise data are available. Thus Hurter has applied (Dynamic Theory of the Manufacture of Sulphuric Acid, S. C. I. 1882, 8, 49, 83) the ordinary dynamical theory of gases to the problem, and arrived at conclusions sensibly according with those arrived at by practical experience as regards the following points:

(1) The work done by a given set of chambers depends upon the quantity of nitre used[1] and the strength of the vitriol made.

(2) The work of the successive chambers of a series decreases nearly in geometric progression, and in consequence the heat development due to chemical action and therefore the excess of temperature of the chambers above their surroundings decrease similarly; whilst the temperature attained in the first chamber relatively to the others depends on the relation between its capacity and that of the whole set.

(3) For a given rate of nitre consumption, and a given mean strength of vitriol made, there is one particular composition of gases which

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[1] [illegible]

will require the minimum total chamber space to cause the conversion of a given fraction of the sulphur dioxide into sulphuric acid.

As regards the first point, the effect of variation in the quantity of available oxides of nitrogen is uniformly to cause a larger production of vitriol in a given space the larger the proportion of such oxides is present relatively to the sulphur dioxide; so that either more sulphur can be burnt in a given time, or a larger fraction of the sulphur dioxide used is converted into vitriol. The more water mist is present (*i.e.* the larger the amount of surface of water particles suspended in the gases) the greater is the amount of action going on in contact with this surface in a given amount of chamber-space in a given time, *cæteris paribus*; whilst the resulting vitriol is the more dilute, at least within certain limits.

As regards the second point, if it be supposed that the gases successively traverse equal amounts of space in passing through the chambers V_1, V_2, V_3......then the amounts of conversion of sulphur dioxide in these respective spaces will form a series of values in geometric progression, *i.e.* in each space the same fraction of the entering gas is converted before passing into the next space; so that with a series of 4 equal chambers, for example, if $\frac{2}{3}$ of the sulphur dioxide entering the first chamber were thus converted into vitriol, and $\frac{1}{3}$ consequently passed on into the next one, $\frac{2}{3}$ of the amount $=\frac{2}{9}$ of the original quantity would be converted into vitriol in this second chamber, leaving $\frac{1}{9}$ of the original quantity to enter the third chamber, in which $\frac{2}{3}$ of this entering amount would again be converted, leaving $\frac{1}{27}$ of the original amount to enter the fourth chamber, and finally $\frac{1}{81}$ of the original amount to escape at the far end; thus

	First chamber	Second chamber	Third chamber	Fourth chamber
Converted .	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{27}$	$\frac{2}{81}$
Escaping unchanged .	$\frac{1}{3}$	$\frac{1}{9}$	$\frac{1}{27}$	$\frac{1}{81}$

Similarly, if the first of a series of 3 chambers caused the conversion of $\frac{3}{4}$ of sulphur dioxide into vitriol, the amounts escaping unchanged would be respectively $\frac{1}{4}$ from the first chamber, $\frac{1}{16}$ from the second, and $\frac{1}{64}$ from the third.[1]

The third point above mentioned may be differently stated, viz. that for a given rate of production of sulphur dioxide, mixed with oxygen and nitrogen so as to produce a burner gas of a given average composition, there is a minimum amount of chamber space requisite (under given conditions as regards nitre consumption relatively to the sulphur burnt and strength of vitriol made) to effect the conversion of a given fraction of the sulphur dioxide employed into sulphuric acid, *i.e.* to reduce the loss by defective conversion to a given limit. The determination of the minimum amount is fixed by the following considerations. In the first place, let it be supposed that the entire chemical change taking place in the burners (using pyrites) is expressed by the reaction

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2;$$

i.e. let the formation of sulphur trioxide be ignored, as also the retention of oxygen in the cinder as sulphates, and the imperfect peroxidation of iron (these suppositions make little difference in the end result, as is shown below). Hence, of the oxygen in the air used to burn the pyrites, part escapes unchanged in the exit gases, and of the balance $\frac{8}{15}$ is used to convert sulphur into SO_2, $\frac{3}{15}$ to oxidise Fe into Fe_2O_3, and $\frac{4}{15}$ for the conversion of SO_2 into sulphuric acid. Now, let the volume percentage of oxygen in air $=a$, and that of nitrogen $=100-a$, and let that of oxygen in the exit gases $=x$, and that of nitrogen $=100-x$, assuming that these gases are made up of nitrogen and oxygen only (*i.e.* that all sulphur dioxide is converted into vitriol). Then the volume of oxygen contained in 100 vols. of air is used up as follows, since sulphur dioxide occupies the same volume as the oxygen contained therein.

In the exit gases	$\frac{x}{100-x}(100-a)$
Conversion of sulphur into SO_2 .	$=\frac{8}{15}\left\{a-\frac{x}{100-x}(100-a)\right\}=\frac{8}{15}\times100\times\frac{a-x}{100-x}$
Conversion of SO_2 into vitriol	$=\frac{4}{15}\times100\times\frac{a-x}{100-x}$
Oxidation of iron in pyrites	$=\frac{3}{15}\times100\times\frac{a-x}{100-x}$
Total	$=a$

The value of a may be taken as 20·9, so that the percentage of nitrogen in air is $100-a=79\cdot1$; if x be taken $=7$, the composition of the burner gas will be as follows:

			In 100 volumes
Nitrogen		79·10	81·54
Sulphur dioxide	$\frac{8}{15}\times100\times\frac{20\cdot9-7}{100-7}$	7·97	8·22
Oxygen in exit gases	$\frac{7}{100-7}(100-20\cdot9)=5\cdot95$	9·94	10·24
Oxygen used to convert SO_2 into vitriol	$\frac{4}{15}\times100\times\frac{20\cdot9-7}{100-7}=3\cdot99$		
Oxygen used to oxidise iron (not contained in the gases) .	=	0	0
		97·01	100·00

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[1] The experiments of Lunge and Naef, since confirmed by other observers, tend to show that in actual practice the proportion of vitriol formed in successive portions of chamber space is only approximately in accordance with that thus theoretically deduced (*v.* p. 747 *et seq.*).

In similar fashion the following compositions of burner gas are calculated for other values of x.

—	$x=4$	$x=5$	$x=6$	$x=7$	$x=8$	$x=9$	$x=10$
Nitrogen . .	81·99	81·84	81·69	81·54	81·38	81·22	81·06
Sulphur dioxide .	9·73	9·24	8·73	8·22	7·70	7·17	6·62
Oxygen . . .	8·28	8·92	9·58	10·24	10·92	11·61	12·32
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

When brimstone is burnt no oxygen is used up in the oxidation of iron, so that of the oxygen not contained in the exit $\frac{2}{3}$ is employed to convert sulphur into SO_2, and $\frac{1}{3}$ to convert SO_2 into vitriol. Hence the oxygen in 100 vols. of air, containing 20·9 vols. of oxygen, is employed as follows:

In the exit gases . . . . $\frac{x}{100-x} \times 79{\cdot}1.$

Conversion of S into SO_2 . . . . $=\frac{2}{3}(20{\cdot}9 - \frac{x}{100-x} \times 79{\cdot}1) = \frac{2}{3} \times 100 \times \frac{20{\cdot}9-x}{100-x}$

Conversion of SO_2 into vitriol . . . . $=\frac{1}{3} \times 100 \times \frac{20{\cdot}9-x}{100-x}$

Whence the following compositions result for different values of x:

—	$x=4$	$x=5$	$x=6$	$x=7$	$x=8$	$x=9$	$x=10$
Nitrogen . .	79·10	79·10	79·10	79·10	79·10	79·10	79·10
Sulphur dioxide .	11·73	11·16	10·57	9·97	9·35	8·72	8·07
Oxygen . . .	9·17	9·74	10·33	10·93	11·55	12·18	12·83
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Here, for a given percentage of oxygen in the exit, the burner gases are some 20 p.c. richer in sulphur dioxide than the corresponding gases from pyrites.

When sulphuretted hydrogen is burnt, oxygen is used up in the conversion of the hydrogen of the gas into water; so that, of the oxygen not contained in the exit, $\frac{1}{2}$ is employed to convert sulphur into SO_2, $\frac{1}{4}$ to convert SO_2 into vitriol, and $\frac{1}{4}$ to burn H_2 to H_2O. If, however, the sulphuretted hydrogen is not pure, but contains a large admixture of incombustible gas (nitrogen and a little carbon dioxide, as in Chance's process) the exit gases will contain this nitrogen &c. as well as that derived from the air. For a given percentage, x, of oxygen in the exit, let m volumes of sulphuretted hydrogen be used per 100 of air, containing n p.c. of H_2S and $100-n$ p.c. of nitrogen; then the total nitrogen in the exit will be $79{\cdot}1 + \frac{100-n}{100}m$. Hence the oxygen in the exit per 100 of air is $\frac{x}{100-x}(79{\cdot}1 + \frac{100-n}{100}m)$. Writing this $=g$ for shortness, the rest of the oxygen is thus employed:

Burning S to SO_2 $= \frac{1}{2}(20{\cdot}9 - g)$
Converting SO_2 to vitriol $= \frac{1}{4}(20{\cdot}9 - g)$
Burning H_2 to H_2O $= \frac{1}{4}(20{\cdot}9 - g)$

Since sulphuretted hydrogen yields its own volume of sulphur dioxide on combustion, which again occupies the same space as the oxygen contained therein, it results that

$$\frac{n}{100}m = \frac{1}{2}(20{\cdot}9 - g)$$
$$= \frac{1}{2}\left\{20{\cdot}9 - \frac{x}{100-x}(79{\cdot}1 + \frac{100-n}{100}m)\right\}.$$

from which the values of m and g are readily calculable for any given values of x and n. For instance, if $x=6$ and $n=33{\cdot}33$, $m=22{\cdot}35$ and $g=6$, and the oxygen is thus employed, the steam produced being left out of the calculation of composition of burner gases.

—	From 100 of air	From 22·35 of sulphuretted hydrogen and nitrogen	Total	
			In burner gases including steam	In 100 volumes
Nitrogen	79·10	14·90	94·00	84·55
Oxygen for burning S to SO_2 .	7·45	—	7·45	6·70
,, ,, H_2 to H_2O .	3·725	—	-	-
,, ,, converting SO_2 to vitriol	3·725	-	9·725	8·75
,, in exit gases . . .	6·00	-		
Sulphuretted hydrogen . . .	—	7·45	-	-
	100·00	22·35	111·175	100·00

Obviously, the greater the value of x the poorer in sulphur dioxide will the burner gases be; whilst the greater the value of n the richer will they be. Even when $n=100$ (pure sulphuretted hydrogen), however, the gases are less rich than when pyrites is burnt, and, *a fortiori*, poorer than when brimstone is burnt; thus when $x=6$, the percentages of SO_2 in the gases are 8·26, 8·73, and 10·57 in the three cases respectively. The following diagram (drawn by Crowther and Cleminshaw, S. C. I. 1888, 172, fig. 6) illustrates the variation in richness of burner gases in SO_2 as n varies, x being $=6$ throughout.

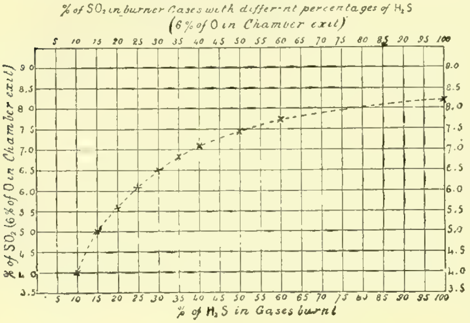

FIG. 6.

The percentage of sulphur dioxide in burner gases from any given source being thus known, the volume of chamber gases containing 1 grm. of sulphur is readily calculable; for this purpose it may be assumed that the mean temperature in the chambers is 50°C., and the mean pressure the ordinary atmospheric one of 760 mm. 32 grms. of sulphur furnish on burning to SO_2 22·4 litres of that gas at 0° and 760° mm., wherefore 1 grm. furnishes 0·7 litre. Hence 1 litre of burner gases at 0° and 760 mm. containing y p.c. of SO_2 by volume will contain $\frac{y}{100\times 0{\cdot}7}=\frac{y}{70}$ grms. of sulphur, or 1 grm. of sulphur will be contained in $\frac{70}{y}$ litres of gas. At 50° this will become $\frac{70}{y}\times\frac{273+50}{273}$ litres measured dry, and when further increased in volume by saturation with aqueous vapour (the tension of which at 50° is 92 mm.[1]) the volume will become $\frac{70}{y}+\frac{273+50}{273}\times\frac{760}{760-92}=\frac{94{\cdot}23}{y}$ litres. The following table gives the values of $\frac{94{\cdot}23}{y}$ for various percentages of sulphur dioxide in burner gases from pyrites and brimstone burners. Similar figures for more or less impure sulphuretted hydrogen are readily calculable when the values of y are calculated as above described.

——	$x=4$	$x=5$	$x=6$	$x=7$	$x=8$	$x=9$	$x=10$
		Pyrites burnt.					
Value of y	9·73	9·24	8·73	8·22	7·70	7·17	6·62
Value of $\frac{94{\cdot}23}{y}$ in litres .	9·68	10·20	10·79	11·46	12·24	13·14	14·24
		Brimstone burnt.					
Value of y	11·73	11·16	10·57	9·97	9·35	8·72	8·07
Value of $\frac{94{\cdot}23}{y}$ in litres .	8·03	8·44	8·91	9·45	10·08	10·81	11·68

It is evident that in all cases, whether pyrites, brimstone, or sulphuretted hydrogen be burnt, the bulk of gas containing 1 grm. of sulphur continually increases with the amount of oxygen contained in the exit gases, *i.e.* with the quantity of additional air mixed with the sulphur dioxide oxygen requisite to form vitriol; and that if this additional air exerted no action other than diluting the active gases, the more concentrated these were (*i.e.* the smaller the value of x) the less space would be requisite to hold the gases containing a given constant amount of sulphur. But in point of fact, this additional air, when not present in too large a proportion, facilitates the carrying action of the oxides of nitrogen, so that, in virtue of this help, the conversion of sulphur dioxide into vitriol goes on more rapidly the more air is present; *i.e.*, so that the gases may be fed into a given chamber-space the more rapidly the greater the value of x without diminishing the yield of vitriol by bringing about a greater proportionate incomplete conversion of sulphur dioxide. Within certain limits the increment in rapidity of feed thus rendered possible with increasing values of x increases more rapidly than does the value of $\frac{94{\cdot}23}{y}$, the volume of gas containing 1 grm. of sulphur; in consequence of which the larger is x the larger is the amount of vitriol that can be made in the chamber-space. Obviously, however, there must be some point where the increased activity due to excess of oxygen no longer exceeds the diminishing effect of dilution, and beyond which further addition of excess of air must diminish instead of increasing the rate of formation of vitriol, so that the rate of feed must be again slackened to admit of the gases remaining in the chamber a longer time so as to effect the conversion of the same fraction of sulphur dioxide as before. In other words, there is some particular value of x in any given case which will enable a maximum rate of feed to be practicable, consistent with a given amount of conversion taking place; or, what is the same thing, there is a particular value of x corresponding with a minimum amount of chamber-space in which the conversion of a given quantity of sulphur dioxide into vitriol can be effected without increasing the loss by deficient conversion.

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[1] As the gases in the chamber are in practice filled with vesicles of dilute sulphuric acid, the tension of aqueous vapour under these circumstances is materially less than 92 mm. (*v.* p. 710 and 727).

The maximum rate of feed thus permissible in a given chamber-space, or the minimum amount of chamber-space requisite for a given amount of production, is necessarily variable with circumstances. Obviously it is largely regulated by the proportionate amount of loss due to defective conversion that is allowed in any given case; the greater the amount permissible *cæteris paribus* the more rapid may be the feed, or the smaller may be the chamber-space. It varies more or less according as brimstone, poor pyrites, or rich pyrites is burnt, and according to the proportion of nitre used and the strength of vitriol made, and is influenced by the consideration as to whether Gay-Lussac and Glover towers are used or not. When rich ores, such as Spanish pyrites, are burnt, the general experience of manufacturers leads to the deduction that even under the most favourable circumstances possible—namely, with Gay-Lussac and Glover towers in thorough working order, and chambers and plant generally of best-proportioned character and in the most efficient state of repair—the daily gas supply must not exceed 10, or at most, 11 times the quantity requisite to refill the chambers when the nitre consumption is nearly at a maximum (about 3 to 4 parts per 100 of sulphur burnt), and the average loss by deficient conversion of sulphur dioxide into vitriol does not exceed 1 or 2 p.c.; whilst with a smaller nitre consumption, 2·5 to 3 parts per 100 of sulphur burnt, about 9 times is more nearly the practical limit[1]; when Gay-Lussac and Glover towers are not used, with a nitre consumption of 10 parts per 100 of sulphur burnt, and a loss by deficient conversion of sulphur dioxide of, say, 5 p.c., the number of times that the chamber-space can be refilled daily cannot exceed 7 or 8; and with a somewhat smaller nitre consumption, 9 parts per 100 of sulphur, 6 to 7 times: provided in all cases that the percentage of oxygen in the exit gases, x, is maintained practically constant at the particular value corresponding with the minimum amount of chamber-space allowable. The value of x which is to be thus maintained is somewhat differently estimated by different authorities; thus Vogt considers that it should not exceed 3 or 4; Schwartzenberg, Bode, and Scheurer-Kestner have assigned values varying between 6 and 6·4; Lunge regards 6·4 as 'very suitable for practical work'; Hurter assumes 6·66 in some of his calculations, but deduces higher values, 6·78 to 10·0, from theoretical considerations,[2] whilst 7 to 7·5 p.c. is allowed by Mactear for chambers in good repair, as much as 11 p.c. being found with old leaky chambers. On the whole, 6·5 may be taken as a value sufficiently near the truth for all practical purposes; with these figures it results from the table given above that the volume of moist chamber-gases at 50°, containing 1 grm. of sulphur, is 11·13 litres. If then this space is refilled n times in 24 hours, it follows that the minimum chamber-space in which 1 grm. of sulphur burnt daily is capable of being converted into vitriol, with the particular plant, nitre consumption, and loss by defective conversion allowed in the different cases just mentioned, must be $\frac{11\cdot13}{n}$ litres; or, what is the same thing, $\frac{11\cdot13}{n}$ cubic metres per kilo of sulphur burnt per 24 hours, or $\frac{11\cdot13}{n}\times 16$ cubic feet per 1 lb. of sulphur burnt per 24 hours.[3]

—	Extreme limit under most favourable conditions possible, and nitre consumption about 3 to 4 parts per 100 of sulphur burnt daily	Gay-Lussac towers used with smaller nitre consumption, 2·5 to 3 parts per 100 of sulphur	Gay-Lussac tower not used; nitre consumption = 9 to 10 parts per 100 of sulphur		
Value of n	11	9	8	7	6
$\frac{11\cdot13}{n}$ = cubic metres per kilo of sulphur burnt daily	1·01	1·24	1·39	1·59	1·85
$\frac{11\cdot13}{n}\times 16$ = cubic feet per lb. of sulphur burnt daily	16·2	19·8	22·2	25·4	29·7

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[1] In some French works a system has been introduced ('production intense' = forced working) whereby nitre recovery plant is employed to [illegible] usual. A greatly increased quantity of nitre is used at first, so as to permit of the accumulation in the chambers of an abnormally large proportion of nitrous fumes relatively to the sulphur dioxide present, these fumes not being lost, owing to the increased dimensions of the Gay-Lussac towers &c. Under such conditions, the rate of gas supply may be largely increased, from 9 or 10 up to something like 15 or 16 times the quantity contained by the chambers per 24 hours (*v.* p. 741).

With Spanish ore yielding 45 p.c. of sulphur as SO_2, and 71·3 p.c. of cinders, the rate of burning and the nitre consumption being constant, and all SO_3 formed in the burner [illegible] from calculations founded on the dynamical theory of gases (*l.c.*), the columns headed 'Ultimate value' being deduced by still further narrowing the calculations.

—	Burner gas		Exit gas	
	Limits	Ultimate value	[illegible]	[illegible]
Nitrogen . .	81·00 to 81·41	[illegible]	[illegible]	[illegible]
Oxygen . . .	12·33 to 10·15	[illegible]	[illegible]	[illegible]
Sulphur dioxide .	6·67 to 8·44	[illegible]		
	100·00 100·00	100·00	[illegible]	[illegible]

[3] The following rules for converting [illegible] expressed on different scales, are given by Hurter. 'To con- [illegible] multiply by 16.' The saltcake made per week is sometimes

Hence under the most favourable conditions possible (probably not easily maintained for long periods together) the minimum chamber-space is about 1 cubic metre per kilo of sulphur burnt daily, or 16 cubic feet per lb.; whilst between 1 and 1·25 cubic metres, or 16 to 20 cubic feet, must be allowed with a lessened nitre consumption, and in view of practical derangements preventing the absolute minimum being attainable for any long period together, even with Gay-Lussac and Glover towers, and otherwise well-designed and well-worked plant. If, on the other hand, these towers are not used, 1·4 to 1·85 cubic metres, or 22 to 30 cubic feet of space, must be allowed, otherwise either the nitre consumption will exceed 9 to 10 parts per 100 of sulphur burnt, or else the loss from defective conversion will exceed 5 p.c. Larger amounts of space still must be allowed if the nature of the ore burnt[1] does not permit of a burner gas being obtained containing an average amount of SO_2 corresponding with 6·5 p.c. of oxygen in the exit gas. For instance, suppose the latter to average 10 p.c. of oxygen, corresponding with 6·62 p.c. of SO_2 in the burner gas, the volume of chamber gases at 50° containing 1 grm. of sulphur is now 14·24 litres. If this chamber-space is refilled 9 times daily, the chamber-space requisite is $\frac{14\cdot24}{9} = 1\cdot58$ cubic metres per kilo = 25·3 cubic feet per lb. of sulphur burnt daily, instead of 1·24 cubic metres or 19·8 cubic feet; and similarly in other cases.

Eschellmann (*l.c. supra*) regards the amount of oxygen in exit gases requisite for best work to be a quantity varying inversely with the nitre consumption and directly with the chamber-space per unit of sulphur burnt; to indicate the connection between the three he gives the following table, to which practical experience has guided him, as necessary to reduce loss by deficient conversion to ·5 p.c. of the sulphur burnt, Gay-Lussac towers being used:—

Chamber space. Cubic metres per kilo sulphur burnt	Oxygen in exit gas	Nitre per 100 of sulphur burnt
1·0	4·5 to 5·0	4·0
1·1	5·0 „ 5·5	3·7
1·2	5·5 „ 6·0	3·5
1·3	6·0 „ 6·5	3·1
1·4	6·5 „ 7·0	2·8

Hurter has calculated the following table to show the variation in the amount of chamber-space requisite to bring about the conversion of a constant fraction (99·5 p.c.) of sulphur dioxide into sulphuric acid, corresponding with given variations in the nature of the burner gases and exit gases under otherwise constant conditions, more especially as regards the proportions between nitre and sulphur burnt and daily consumption of pyrites. It is here assumed that 16 cubic feet of space per 1 lb., or 1 cubic metre per kilo, of sulphur burnt daily, will suffice to bring about the conversion of 99·5 p.c. of the sulphur dioxide into vitriol, when the exit gases contain 6·66 p.c. of oxygen, representing 8·5 p.c. of sulphur dioxide in the burner gases, using Spanish pyrites, and making vitriol of constant strength throughout, with the aid of Gay-Lussac towers.

Per cent. SO_2 at inlet	Per cent. oxygen at outlet	Cubic feet per 1 lb.	Cubic metre per kilo	Total loss if only 1 cubic metre (or 16 cubic feet) available
4	14·77	41·00	2·563	15·66 p.c.
5	13·05	28·33	1·771	5·03 „
6	11·30	21·76	1·360	2·03 „
7	9·5	18·14	1·134	0·93 „
7·5	8·56	17·04	1·065	0·69 „
8	7·62	16·33	1·021	0·55 „
8·5	6·66	16·00	1·000	0·50 „
9	5·69	16·09	1·006	0·52 „
10	3·70	18·08	1·130	0·92 „
11	1·61	28·03	1·752	4·88 „

The last column shows the relative amounts of loss through incomplete conversion of sulphur dioxide into vitriol that would occur if only 16 cubic feet per lb. (or one metre per kilo) of space were available throughout, that occurring under the most favourable conditions being 0·50 p.c.; obviously but little practical difference is here represented as being caused by very considerable fluctuations in the character of the burner and exit gases, as long as these variations are not outside the limits of 7 to 10 p.c. of sulphur dioxide in the former, or 3·7 to 9·5 p.c. of oxygen in the latter; but as soon as these limits are passed, a very rapid increase in the amount of loss is at once noticeable.

The following practical case within the author's own experience illustrates the effect of deficient chamber-space very completely. In a works making acid without Gay-Lussac and Glover towers and employing some $\frac{5}{6}$ of the total pyrites burnt in the form of Spanish ore, and $\frac{1}{6}$ of Wicklow pyrites containing about 30 p.c. of sulphur, the yield of acid during a

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employed for calculations instead of sulphur burnt; in this case, 'cubic feet per ton of saltcake per week is 75 times the cubic feet per pound of sulphur per 24 hours; and 1,200 times the cubic metres per kilo. of sulphur per 24 hours.'

[1] Favre found that when 40 p.c. pyrites was used in a works in the South of France, the chamber-space was 1·66 cubic metres per kilo of sulphur charged into burners, representing about 1·8 cubic metres per kilo actually burnt, or 28·8 cubic feet per pound of sulphur burnt daily.

particular period was distinctly below the normal amount owing to the chamber-space being already too small to permit of the loss by defective conversion being reduced to as low a limit as 5 p.c., to effect which *at least* 22 to 25 cubic feet of space per pound of sulphur burnt daily would have been requisite. With the intention of increasing the production, the chambers were still further forced by burning more pyrites and adding a somewhat larger proportion of nitre; with the result of greatly intensifying the relative amount of loss by defective conversion.

—	Cubic metres of chamber space per kilo of sulphur charged into kilns daily[1]	Cubic feet per pound of sulphur	Nitre per 100 parts of sulphur charged into kilns	Sulphur converted into vitriol per 100 parts charged into kilns	Total loss
1st period .	1·150	18·4	9·31	81·5	18·5
2nd „ .	1·073	17·2	9·84	75·4	24·6
3rd „ .	1·017	16·3	10·02	68·4	31·6

[1] When chamber space, nitre, &c., are reckoned per 100 parts of sulphur *charged into kilns*, the figures are necessarily smaller than those calculated per 100 parts *sulphur burnt* by an amount proportionate to the quantity of sulphur left unburnt in the cinder—as a rule, about 5 or 6 parts per 100 charged into kilns, with Spanish ore.

Of the 'total loss' about 7–7·5 parts throughout are due to the unburnt sulphur left in the cinder, taking the two kinds of ore burnt together, so that the losses by leakage and defective conversion jointly are about 11, 17, and 24 p.c. of the sulphur charged into the kilns in the three periods respectively, notwithstanding a progressive increment in nitre consumption. Of the relatively enormous increase in loss here observable, doubtless part was due to increasing leakages through defective repair as the chambers grew older (some being nearly worn out even during the first period); but the majority was due to the decrease in amount of chamber space available relatively to the volume of burner gases supplied, outside of those limits within which such decrease would only produce a comparatively small effect on the yield.

When brimstone is burnt, owing to the greater richness of the burner gases, it is generally considered that a smaller excess of oxygen is requisite than in the case of pyrites[1]; admitting that an exit gas containing 5 p.c. of oxygen is now the best proportion, it results from the table given above that the volume of chamber gases at 50° containing 1 grm. of sulphur will be 8·44 litres. If the nitre consumption (with Gay-Lussac towers) be comparable with that in the case of pyrites—*i.e.* about 3 to 4 parts nitre per 100 of sulphur burnt—the maximum number of times the chambers can be refilled with gases daily will be about the same as in that case, viz., about eleven times under the most favourable conditions possible, or nine times with smaller nitre consumption and allowing for unavoidable irregularities; corresponding respectively with $\frac{8\cdot44}{11} = \cdot77$ and $\frac{8\cdot44}{9} = \cdot94$ cubic metres per kilo, or 12·3 and 15·0 cubic feet per lb., of sulphur burnt daily. Brimstone chambers, however, are, in Europe at any rate, usually erected on a smaller scale than pyrites chambers, and therefore cool more rapidly, so that, especially in winter, the mean temperature of the gases is often sufficiently lowered to exercise an appreciable retarding influence on the rate of formation of vitriol. Moreover, they are comparatively seldom fitted with Gay-Lussac towers, whilst a much smaller proportion of nitre is usually employed than with pyrites chambers under similar conditions—viz. from 5 to 8 parts with an average of, say, 6·5 per 100 of sulphur burnt instead of 10 parts—the result of which difference is that, instead of the chambers being refilled some seven or eight times in twenty-four hours, they are usually only refilled from four to six times, thus giving $\frac{8\cdot44}{4} = 2\cdot11$ to $\frac{8\cdot44}{6} = 1\cdot41$ cubic metres per kilo, or 33·8 to 22·6 cubic feet per pound, of sulphur burnt daily, with which amounts of chamber space the loss by defective conversion may be reduced to amounts not exceeding 5 or 6 p.c., and sometimes considerably less with careful working.[1]

When diluted sulphuretted hydrogen is burnt (*e.g.* gas obtained by Chance's process, consisting of about one-third sulphuretted hydrogen and two-thirds nitrogen), the burner gas contains, as above shown, considerably less sulphur dioxide for a given amount of oxygen in the exit than pyrites burner gases, viz. 6·70 p.c. instead of 8·73 for an exit containing 6 p.c. of oxygen; and consequently the minimum chamber-space requisite might be expected, *a priori*, to be $\frac{8\cdot73}{6\cdot70} = 1\cdot30$ times that necessary for pyrites, all else being the same. According to A. M. Chance (C. S. I. 1888, p. 168), the chamber-space required with such sulphuretted hydrogen 'corresponds to our ordinary standard of chamber-space used at our works for many years past in burning Spanish pyrites,' when Gay-Lussac and Glover towers were used, and nitre equal to 2·9–3·6 parts per 100 of sulphur burnt, 98–99 p.c. of the sulphur burnt as sulphuretted hydrogen being obtained in the form of vitriol, working at a rate sufficient to make acid containing 40 tons weekly of SO_3, or about 50 tons of oil of vitriol, or 60 of acid at 150° T. The experience of other manufacturers, however, has usually not been quite so favourable; possibly on account of irregularities in the sulphuretted hydrogen supply and the presence therein of carbon dioxide.

In the preceding calculations it has been assumed that certain corrections might be neglected without materially influencing the results. The following considerations will show that, on the whole. these various corrections do, in fact, approximately balance one another. In the first place, the gases are increased in volume by the oxides of nitrogen present not taken into account. Again, if the factory is situated above the sea-level, the average atmospheric pressure will be more or less below 760 mm., thus increasing the volume of gas containing 1 grm. of sulphur. According to Lunge, a difference of 5·5 p.c. in the volume occupied by a given quantity of gas exists due to this cause according as the gas is at Munich or Marseilles, the temperature being the same. In summer, moreover, the mean temperature of the gases is higher than in winter, and the volume occupied relatively greater; in consequence, if the output from a given amount of plant remains the same, the yield from a given quantity of materials is diminished from the effect of relative diminution in working space.[1] Nextly, in the case of pyrites, a certain amount of *sulphate* is always formed and retained by the burnt ore, leading to a diminution in the total oxygen contained in the gases relatively to the nitrogen, or, what is the same thing, to an increment in the bulk of gas containing a given weight of sulphur proportionate to the additional diluting nitrogen thus introduced. The extent of this dilution, however, is rarely great. Thus, supposing the burnt ore to contain sulphates equivalent to 3 p.c. of SO_3, *i.e.* containing 1·8 p.c. of oxygen thus combined, an amount considerably beyond that usually present in burnt Spanish ores or similar pyrites containing little or no lime, or other bases forming sulphates less easily decomposed by heat; since the burnt ore weighs about $\frac{2}{3}$ of the pyrites used, the oxygen present in this quantity of SO_3 will be $\frac{2}{3} + 1\cdot8 = 1\cdot2$ parts per 100 parts of original pyrites, which latter would require, at 48 p.c. sulphur, $48 \times \frac{11}{8} = 66$ parts of oxygen, assuming the sulphur to be all present as FeS_2 and to be completely converted into Fe_2O_3 and SO_2; so that the amount of oxygen requisite for oxidation would be increased by $\frac{1\cdot2}{66}$, or distinctly less than 2 p.c., by this formation of sulphates; wherefore the volume of burner gases containing a given weight of sulphur could not be increased as much as 2 p.c. by this action. A similar small incremental correction is due for oxygen taken up in oxidation of zinc, lead, arsenic, &c., which consume somewhat more oxygen to form metallic oxide and SO_2 than does FeS_2 containing the same weight of sulphur.

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[1] Hurter [illegible] sli[illegible] for [illegible] of oxygen in the [illegible] SO_2 in the burner [illegible].

[1] [illegible] proper proportion for a small set of chambers without Gay-Lussac towers, using 6 p.c. of nitre; in larger works 22·8 [illegible] much more nitre was requisite or else acid was largely lost.

These various corrections jointly would increase the value of $\frac{94\cdot23}{y}$ by some few per cents.; on the other hand, three other corrections would slightly tend to reduce it. The first of these is the circumstance that more or less sulphur trioxide is always contained in the burner gases; it is impossible to form an accurate estimate of the average amount so contained, but certainly it does not amount to as much as one-fifth of that corresponding with the total sulphur burnt.[1] Assuming this figure, however, and admitting that the exit gases contain 7 p.c. of oxygen, the air entering the burner will be employed as follows:

Nitrogen	79·10
Oxygen in exit gases . .	5·95
Oxygen employed in oxidising iron of pyrites . . .	2·99
Oxygen employed in converting sulphur into SO_2	7·97
Oxygen employed in converting one-fifth of the SO_2 into SO_3 in the burners . . .	·80
Oxygen employed in converting four-fifths of the SO_2 into vitriol in the chambers . .	3·19
	100·00

Hence the burner gases, excluding SO_3, will consist of:

		In 100 vols.
Nitrogen . . .	79·10 =	83·60
Oxygen . .	$5\cdot95 + 3\cdot19 = 9\cdot14 =$	9·66
Sulphur dioxide	$\frac{4}{5} \times 7\cdot97 = 6\cdot38 =$	6·74
	94·62	100·00

and consequently the volume of gas containing $\frac{4}{5}$ grm. of sulphur, corresponding with 1 grm. actually burnt, will be $\cdot8 \times \frac{94\cdot23}{6\cdot74} = 11\cdot18$, or not quite 3 p.c. less than the value 11·46 deduced above when the formation of SO_3 is not taken into account. This fraction, under 3 p.c., is obviously overstated, because the conversion of SO_2 into SO_3 in the burner is actually less than 20 p.c., and because the SO_3 vapour produced occupies space not allowed for. The second correction is the circumstance that burnt pyrites often contains a small fraction of the iron in forms of oxidation lower than Fe_2O_3, so that the oxygen taken up by the iron is rather over-stated. In the third place, the volumes of gas containing 1 grm. of sulphur at 50°C. and 760 mm. are not quite correctly stated by the formula $\frac{94\cdot23}{y}$, because the assumed tension of aqueous vapour at 50° is greater than that really exerted in the chambers on account of the influence of the vesicles of vitriol in diminishing the tension; and consequently 94·23 is slightly too high a value.[2]

Taking all the corrections together, it may reasonably be concluded that they balance one another sufficiently nearly to warrant the deduction that the minimum chamber space essential for proper continuous working under the most favourable conditions possible is that above deduced—viz., from 1 to 1·25 cubic metres per kilo

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[1] Possibly also because the higher average temperature facilitates those secondary reactions that interfere with the cycle of operations effected by the oxides of nitrogen by destroying the 'available' oxides—*i.e.* by reducing them to nitrous oxide or free nitrogen.

[1] In specially conducted laboratory experiments Lunge obtained figures representing 18 p.c. as a maximum for the sulphur converted into SO_3 by roasting pyrites and passing the gases over hot ferric oxide; but this value is greater than anything that could be formed in actual pyrites burners where the gases pass through much less ignited ferric oxide than in these experiments. Much smaller values, down to 3 or 4 p.c., have been observed by other experimenters (Fortmann, Bode, Scheurer-Kestner and others). Even when sulphur is burnt in a glass tube in a current of air, a small quantity of trioxide is formed, about 2 or 3 p.c. of the sulphur being thus oxidised, according to Lunge.

[2] For table of tension of aqueous vapour emitted by dilute sulphuric acid, *v. supra*, p. 710.

(16 to 20 cubic feet per pound) of sulphur burnt from Spanish pyrites in twenty-four hours; but that very considerably larger amounts are requisite when the conditions are less favourable if the fraction of sulphur converted into vitriol is to be the same; or, conversely, that unless very considerably larger amounts of space are allowed, a notably smaller proportion of sulphur becomes transformed into vitriol—*i.e.* the loss from incomplete conversion becomes materially increased. The actual amount of loss from this source permissible (apart from that due to leakages, &c.) is, of course, very much a matter of judgment in each particular case. Working under the best conditions (*e.g.* with Gay-Lussac and Glover towers in good order), the loss need not exceed an average of 1 or, at most, 1·5 p.c. of the sulphur burnt over long periods of time, this limit including the higher losses necessarily occurring from unavoidable accidents, and for a little while after stoppages for repairs &c. on re-starting the plant. Thus Mactear gives the following figures obtained in a large works having a number of series of chambers (Journ. Soc. Arts, vol. 26, 1878, 556), the larger numbers obtained during the earliest period being due to the circumstance that a systematic testing of the escaping gases was then just being introduced, by means of which the occurrence of occasional abnormally large escapes was rendered evident, and thus a better method of working for preventing such irregularities was rendered possible, in a way impracticable when simple inspection of the chambers was relied on as a criterion of proper working. Gay-Lussac towers were used, and the chamber space was 20 cubic feet per pound of sulphur burnt daily.

Sulphuric acid (H_2SO_4) lost per 100 lbs. of sulphur burnt

—	Maximum	Minimum	Average	Percentage of original [illegible] burnt lost by incomplete conversion
1st month	26·96	1·00	7·00	2·33
2nd ,,	10·60	·80	2·96	·97
3rd ,,	29·75	·80	4·21	1·37
4th ,,	8·30	·40	2·37	·77
5th ,,	2·60	·50	1·68	·55

The last column is derived from the average monthly loss expressed in H_2SO_4 by multiplication by $\frac{32}{98}$, so as to translate the figures into sulphur values. When a proper system of testing for escapes is employed, according to Mactear, 'there is no insuperable difficulty in keeping down the escape of the sulphur acids to 2·5 p.c. H_2SO_4 on the sulphur burnt'—*i.e.* to ·81 p.c. of the sulphur itself. When, however, less care in supervision is exercised—and especially when the chamber-space is not well outside the limiting minimum compatible with good work irregularities in working are apt to occur, which, for the time being, cause relatively large amounts to escape, and this materially increases the average loss over a long period of time. Under such circumstances an average loss (apart from leakages and accidents) of 4 or 5 p.c. of the sulphur burnt (and even more) [illegible]

When working under comparatively unfavourable conditions, and especially when Gay-Lussac and Glover towers are not used, the loss by defective conversion is usually considerably greater than under better conditions, partly because the chamber-space available relatively to the sulphur burnt is frequently insufficient to effect as large a proportion of conversion, partly because unless an unduly large proportion of nitre is used a larger surplus of sulphur dioxide is generally of necessity present in the last chamber of the series. With comparatively new chambers in good condition, the loss from leakages and defective conversion jointly may be brought down to 5 or 6 p.c. of the sulphur burnt, provided that the chamber-space is not too small (say 25 cubic feet per 1 lb. burnt daily), and that due care in avoiding irregular working is exercised; but 10–12·5 p.c. ($\frac{1}{10}$ to $\frac{1}{8}$) as the average loss for long periods of time from these two causes jointly is much nearer the practical result actually obtained, and in some cases as much as 15, and even 20, p.c. and upwards of loss is incurred; partly because insufficient chamber space is allowed; partly because, through false economy, large amounts of leakage through defective repair take place; and largely because the system of management which dispenses with modern improvements, such as Gay-Lussac towers and scientific skill in their use, is very apt to rely on 'rule of thumb' working, leading to considerable irregularities and consequent losses by defective conversion.

Various proposals have been made to modify the general arrangement of chambers and subsidiary plant in certain ways so as to obtain the same output of vitriol with a greatly decreased cubic capacity. One of the most effective of these is the method of 'forced working' ('production intense,' p. 737, footnote) used in some French works, whereby an increased amount of nitre is allowed, mostly recovered by means of larger Gay-Lussac and Glover towers, so that a greatly increased amount of nitrous fumes is always in circulation. In this way, as little as 12 cubic feet is requisite per pound of sulphur. Another method that has been found effective in practice is the use of 'plate columns' in combination with ordinary chambers (*v.* p. 748).

8. **Chambers: details of construction and working &c.** Although the total amount of chamber-space required for a given rate of production under given conditions, so as to work to the best advantage, is regulated as above described within tolerably narrow limits, the same can by no means be said of the form and disposition of chambers relatively to one another calculated to give the best results. Obviously the maximum amount of capacity relatively to the lead surface would be attained in a sphere, a shape practically out of the question on account of the difficulty in erecting staging. Cubical vessels of 40 feet and upwards on the side have been used, with the view of diminishing as much as possible the lead requisite. For much the same reasons Hasenclever has recommended chambers some 33 feet high and the same in width, with a length of 130 feet or so, giving a cubic capacity of about 140,000 cubic feet. Nar- [illegible] length, up to 200 or 300 feet, have also been em-

ployed by some. From observations of his own H. A. Smith has deduced the conclusion that the best form of chamber is 150 feet long, 25 to 30 wide, and 10 to 12 high. In general, however, chambers of 100–130 feet long, 25–30 wide, and 16 to 20 high, are preferred, giving a capacity of 40,000 to 80,000 cubic feet. In some cases a series of chambers, through which the gases pass consecutively, is employed, especially when a Glover tower is used at the entrance end and a Gay-Lussac column at the other; whilst another arrangement much in vogue is one where two or more 'working' chambers are each provided with burners, the gases from each either uniting at once, and passing through other 'receiving' chambers together, or being passed through intermediate separate chambers, and then uniting to pass through a final 'exhaust' chamber. Lunge states that at Uetikon, and also in France, an arrangement that has been adopted with great success is to use three chambers in succession, the first of which has a cubic capacity equal to two-thirds of the whole, the second two-ninths, and the third one-ninth. Two rules have been arrived at by practical experience bearing on the point: one is that the dimensions of each chamber should be such that for every cubic foot of space there should be not far from ·2 square feet of total surface, including top, bottom, sides, and ends; thus a chamber 20 × 25 × 100 feet contains 50,000 cubic feet, and has a total surface of 10,000 square feet, giving the ratio ·2 exactly. The other rule is that when the total chamber-space is large, it is better to break it up into two or more different sets of chambers, worked entirely apart from one another, each having a cubic capacity of 150,000 to 200,000 cubic feet, than to pass the whole bulk of gases through the same final chambers or exhausts; for were this done, the velocity of passage of the gases through these last chambers would be too great to allow of proper time for action being given, whilst the Glover and Gay-Lussac towers would either have to be of enormous size (in which case effective working becomes far more difficult) or else must still be erected in duplicate or triplicate; so that nothing is gained, but a good deal may be lost, by such a mode of working.[1] Thus a series of four chambers, the first three of which measure 20 × 25 × 100 feet, giving a capacity of 50,000 cubic feet each, whilst the fourth exhaust chamber is somewhat smaller (say 35,000 cubic feet), would be competent to deal with the gases from two sets of 14 kilns each, in each of which 28 kilns 7 cwts. of 48 p.c. pyrites is burnt daily. A little upwards of 10,500 lbs. of sulphur is thus charged daily into the kilns, of which about 10,000 lbs. are actually burnt; so that, as the chamber-space is altogether 185,000 cubic feet, about 18·5 cubic feet are allowed per lb. of sulphur burnt daily. One ordinary-sized Glover tower and one Gay-Lussac column of dimensions not too large for good work would be employed with this set. Nearly the same result as regards relation between chamber-space and sulphur burnt would obviously be attained by the use of six equal chambers in succession, each having a capacity of 30,000 cubic feet—a mode of arrangement which has been adopted with satisfactory results when 20 cubic feet of space were allowed per lb. of sulphur burnt daily, the loss of sulphur dioxide by incomplete conversion being less than 1 p.c. when the plant was carefully worked and the escapes determined regularly by special methods (Mactear, Journal Soc. Arts, May 17, 1878).

When a series of chambers is used, they are usually arranged so that each is a few inches higher than the preceding one, in order to enable the weaker acid produced in the last chamber (which contains most oxides of nitrogen dissolved therein) to flow regularly back through the series, all acid being withdrawn for use from the first chamber, unless there is some reason to the contrary. Mactear (*l.c.*) advocates passing the first chamber acid back to the exhaust again, so that the sulphur dioxide contained in the strongest acid may reduce the nitric acid apt to be formed in the weakest acid, and thus diminish corrosion of lead. This necessitates the use of some form of acid pump to raise the liquid the requisite height; but the extra cost is much more than repaid by the diminution of wear and tear of lead effected, whilst a substantial reduction in nitre consumption is possible, as active oxides of nitrogen are thus returned to the atmosphere of the chamber instead of being retained in the acid, and considerably stronger vitriol may be safely manufactured in the last chamber, viz., 10°–15°Tw. higher than previously, when the last liquor was 90°–100°Tw.

Chambers are usually constructed of sheet lead, of such thickness as to weigh 6 lbs. per square foot, although sometimes rather stouter lead is used (7 or even 8 lbs.), especially for the earliest in the series, which being the hottest are therefore the most readily attacked. In America 5-lb., or even 4-lb., lead is sometimes employed. F. Bode (Zeits. f. angew. Chem. 1889, 357; also S. C. I. 1889, 774) finds that if the weight of lead requisite for making the actual surface of the chambers (without considering that used for internal fittings) be taken as unity, then (reckoning the metal to weigh 32·5 kilos. per square metre = about 6½ lbs. per square foot) the distribution of total lead used in three different works was

——	A	B	C
Chambers	1·40	1·37	1·33
Towers	·25	·19	·29
Remaining plant	·14	·13	·18
Total	1·79	1·69	1·80
Capacity of chambers in cubic metres	5800	4550	2265
Lead used in metric tonnes	238	160	96·2

The walls and roof are supported by a stout scaffolding of beams and joists, well mortised together, forming a skeleton of vertical and horizontal wooden bars, to which 'straps' of sheet lead are fastened by iron nails, coated with lead at the heads to enable them better to resist corrosion. These straps are fused to the sheet-lead itself by means of a special form of blowpipe burning hydrogen, and urged by a blast of air from a bellows. Usually the sheets themselves are similarly fused together at the edges, so as to dispense with solder, but sometimes unfused 'rabbet' joints are employed, made by folding the edges over and then beating down flat. The roof and sides, or *curtain*, of a chamber is thus constructed practically all of one piece. The bottom is sometimes also fused to the sides, so that the whole chamber forms one gigantic water- and gas-tight leaden box; but more frequently the curtain hangs down into a large flat dish or 'saucer,' made by turning up the edges of the bottom 12 or 15 inches, this saucer being kept filled several inches deep with chamber acid when the chambers are working; the dependent curtain dips into the acid all round, so as to make an hydraulic lute.

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[1] During temporary derangements for repairs &c. it may often be necessary to carry the gases from one set into another to utilise them and prevent the unaffected portion of the set from lying idle.

In Britain chambers are usually built freely exposed to the weather, excepting in so far as shingling is sometimes built round the supporting scaffolding to prevent damage by wind; the roofs are then constructed on a slight slope, one side being a few inches higher than the other, so that rain runs off into a gutter, so fixed as to prevent it running down into the turned-up edges of the saucer; or the centre is made higher than the sides, each of which is then guttered. In hotter climates boarding to keep off the sun and prevent access of rain is much more frequently used; and, similarly, in colder localities, to prevent undue chilling in winter. The whole structure is almost invariably supported upon brick or stone walls or piers, or, better still, on cast-iron columns, so that a large amount of space is gained underneath, utilised for the erection of the kilns, nitre ovens, &c., for storing and breaking up pyrites, and such like purposes. In this way the kilns are not only protected from the weather, but also, to a great extent, from the effect of wind, which would be apt to render the draught irregular were they built in the open. On the supporting walls, columns, or arches rests the 'sill,' a rectangle of stout beams, indicating the outline of the chamber, carrying the transverse joists or girders which support the saucer, so arranged as to distribute the weight uniformly. These joists usually project outwards several feet, so as to carry an outside gallery affording access to the edges of the saucer for sampling, drawing off liquor, and generally testing the working of the chamber. Vertical 'standards,' mortised into the sill and stayed together transversely, support the 'capping,' another stout rectangle carrying the transverse rafters to which the roof is attached. When the width of the chamber is considerable (upwards of 30 feet), trussed beams or girders are generally used, some 20 feet apart, provided with iron loops bolted thereto, which support the rafters, in this case running longitudinally, and not transversely. The lower joists are boarded over like an ordinary room, so as to support the saucer at all points and prevent cutting by the edges of the joists and consequent leakage; the upper ones are usually not boarded, the leaden roof being simply supported from them by means of straps.

When a series of chambers is used each one is connected with the one before and behind by a 'tunnel'—*i.e.* a square tube of sheet-lead, supported by a wooden framework, like a miniature chamber; or a circular one, held up by iron rings, &c. According to Schwarzenberg's experiments, the best arrangement is for the gases to leave one chamber at the bottom and enter the next at the top, thus necessitating the tunnel to pass upwards. In this way the least interference with the draught is occasioned, whilst the opposite would be the case were the gases withdrawn at the top and made to enter at the bottom. In practice, however, ascending tunnels are rarely used,[1] horizontal ones connecting the chambers at such a level as to be easily accessible for inspection from the galleries running round the base of the chambers being generally preferred—*i.e.* the centre of the tunnel being some 4 or 5 feet above the floor of the chamber. It is quite possible that a certain amount of virtual loss of space is thus occasioned, the draught not much affecting the portion of the earlier chamber below the level of the tunnel at the far end, and thus rendering that part less practically efficient; but the greater convenience outweighs this slight drawback. According to Lunge and Naef's experiments, it is practically indifferent where the connecting tubes are placed, so far as the formation of vitriol is concerned. When a Glover tower is not used, a cooling-pipe is generally employed to prevent the burner gas reaching the first chamber at too high a temperature. This is usually a large cast-iron pipe, 2 or 3 feet diameter, and of length sufficient to enable the cooling action of the air to reduce the temperature to the required extent, preferably to not higher than 60°C. or 70°C. Occasionally other means of chilling—such as a water-jacket—are employed. Sulphuric acid frequently condenses in the liquid state in the pipes, and runs out from the joints. This concentrated acid is generally used up for the nitre-pots. A sufficiently long pipe usually renders a dust-depositing chamber unnecessary; but when a Glover tower is employed such a chamber (usually a large expansion of the flue) is eminently desirable, if not indispensable, as in that case the burner gases are led directly into the tower without passing through cooling pipes, so that all dust carried with the gases finds its way into the tower and consequently into the acid passing through it. The cooling caused by the evaporation of water from this acid suffices to reduce the temperature of the issuing gases without any other chilling appliances being required. Sometimes a small leaden chamber not fed with steam is used as a preliminary dust-depositing vessel.

On first starting a new chamber, the saucer should be filled up so as to lute the curtain with acid already prepared, and not with water; were the latter employed, great loss of nitrous fumes would be occasioned by their absorption in the water and destruction through the increased amount of secondary reaction brought about (*v.* p.

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[1] In the case of the first chamber of a series it is usual to [illegible] the Glover tower.

730). Moreover, corrosion through formation of nitric acid in the aqueous solution would be rendered imminent. Even when closed chambers are used (sides fused to bottom instead of saucer), it is usually preferred to start with a depth of some inches of acid in them; but if acid is not at hand for the purpose, starting dry is preferable to introducing water. In order to test the working, tell-tales are provided, consisting of earthenware or leaden funnels supported inside in different parts of the chamber mouth upwards so as to catch the precipitated globules of acid, precisely after the fashion of a rain-gauge; leaden tubes passing through the wall enable the 'drips' to be collected and tested as to their strengths by means of an hydrometer. In the same way, gutters running slopingly along the inner wall enable samples to be taken of the liquid condensing on the sides of the chamber. Ordinarily these latter samples show at any given moment a considerably lower sp.gr. than the former ones, on account of the greater condensation of aqueous vapour by contact with the surface cooled by the external air; for this reason the drips are almost invariably stronger than the average acid contained in the saucer (sampled through a small man-hole for the purpose). When a series of chambers is used, moreover, the acid condensed in the later ones is generally weaker than that formed in the earlier ones; as the liquor runs back from the later to the earlier ones by gravitation, the average bottom liquor is further weakened through this cause.

W. Crowder (S. C. I. 1891, 295) finds it preferable, instead of testing drips from the sides of chambers, *to collect those from the connecting pipes.* Such drips, for a series of four chambers, should have the following gravities when the working is normal:—

Drip from tower to 1st chamber	95° to 104°Tw.
,, No. 1 to No. 2 ,, . .	130°
,, No. 2 to No. 3 ,, . .	122°
,, No. 3 to No. 4 ,, . .	105°
,, No. 4 to Gay-Lussac . .	85°

An increased consumption of nitre was always observed when the drip from No. 1 to No. 2 stood below 130°.

The admission of steam is mainly regulated in accordance with the gravity indicated by these samples and that possessed by the bottom acid, being partly cut off if the liquid is too dilute, and *vice versâ.* In general, the English custom is to make the chamber acid run off for further concentration in the Glover tower &c., or for immediate use, of about the sp.gr. 1·600–1·625 (120–125° Twaddell); but notably lower strengths (110–115°Tw.) are often used abroad. If the strength exceeds about 125°Tw. (sp.gr. 1·625), the quantity of nitrous fumes dissolved in the acid begins to increase very considerably, and the rate of wear of the chamber through corrosion &c. is notably more rapid than when not above this limit; whilst an increased amount of evaporation is rendered necessary if the strength falls largely below 120°. Owing to the dilution of the acid from the causes above mentioned, the drip in the first chamber (from tell-tales not placed against the wall so as to collect the weaker liquor running down the sides, but well inside and near to the entrance of the burner gases) usually indicates some 10–15°Tw. higher gravity—*i.e.*, the drip in the first chamber of a series usually indicates about 132–138°Tw. at this point, and somewhat less at the far end; in the subsequent chambers the difference between the drip and bottom acid is generally not quite so marked, about 5–10°Tw. According to Lunge, the practice of most German and Austrian works, where all the processes are checked with the greatest care and the work carried on in the most perfect style practicable, is that the strength of the acid drawn off from the leading chamber shall not exceed 113°Tw., and is best kept at 106° to 110°Tw., if the best yield and minimum consumption of nitre is aimed at. On the other hand, several works in Lancashire have, since 1889, begun to work with much stronger acid in the leading chamber—up to 140°; with the result of obtaining 41½ cwt. of 96 p.c. saltcake per ton of pyrites, with a consumption of only 15 lbs. nitre (about 2·6 lbs. per 100 of sulphur burnt), 17 cubic feet of space being allowed per lb. of sulphur. The increased wear and tear thus brought about is regarded as more than compensated by the saving in the process. The strength of the acid produced in the subsequent chambers varies much in different works, more especially according as a Gay-Lussac tower is used or not; in the former case less steam is usually admitted to the later chambers than in the latter, so that the acid made will frequently not fall below 100°Tw. even in the final exhaust chamber, and will mark between 110° and 120° in intermediate chambers; whilst when no Gay-Lussac tower is used the acid made in the exhaust chamber is frequently so much diluted by using excess of steam as not to indicate more than 50° or 60°Tw., and sometimes considerably less. Practice varies, however, so much in this matter that no definite figures can be quoted as those usually adhered to. The weaker the acid made, the greater is the amount of destruction of available nitrogen oxides by reduction to nitrogen or nitrous oxide. Moreover, the available oxides are more or less converted into nitric acid when in presence of much water and oxygen, thus

$$4NO + 3O_2 + 2H_2O = 4HNO_3$$
$$N_2O_3 + O_2 + H_2O = 2HNO_3;$$

so that much corrosion is brought about by the presence of nitric acid in the weak vitriol formed.

In addition to frequent examination of the drip and bottom acid for the purpose of regulating the steam supply, the colour of the gases in the chambers requires continuous inspection in order to see if the right proportion of nitrous fumes is present; this inspection is made by looking through glass windows let into the walls of the chamber and connecting tunnels, either horizontally towards another window opposite, or diagonally upwards towards a 'sight' in the roof, conveniently made by arranging an hydraulic lute covered with a bell-jar so as to afford easy access to the interior for sampling, &c., if required, as well as acting as a skylight. When Gay-Lussac towers are used, the last chamber should show a pretty deep ruddy tint, indicating that practically all sulphur dioxide has become converted into vitriol, and that the nitrogen oxides are essentially those higher than NO. Should material paling in tint be visible at any time, it indicates that more or less sulphur dioxide in excess of the normal small quantity is present, and in consequence that more or less considerable loss may be occasioned, not only from escape of sulphur dioxide in the waste gases, but also through imperfect absorption of nitrogen oxides in the Gay-Lussac tower, any NO present passing through unabsorbed. In the earlier chambers the red colour is far less pronounced, inasmuch as at any given moment a much smaller proportion of the nitrogen oxides present exist as N_2O_3 or NO_2 than in the exhaust. The precise shade, of course, to some extent depends on the thickness of the stratum viewed; a peculiar mistiness due to the effect of the suspended vesicles of liquid acid always complicates the visible effect, a diminution in this, rendering the gaseous atmosphere more transparent, being one of the indications of deficient steam supply. When Gay-Lussac towers are not used, the colour of the gases in the exhaust chamber is much paler than when they are employed, partly because the total quantity of nitrogen oxides is then less in proportion to the sulphur dioxide (notwithstanding the larger nitre consumption) on account of the absence of the cumulative action effected by the towers, partly on account of the greater condensation of these oxides in the weaker acid made through the larger steam supply, owing to their conversion into nitric acid as above.

In the French 'forced' style of working (p. 737), the gases in the last chamber are much more deeply tinted, and usually contain N_2O_4 as well as N_2O_3 and NO.

Besides the sp.gr. tests applied to the drips and bottom acid in the various chambers, it is generally useful to test these from time to time as to the amount of nitrogen oxides present. If the strongest does not exceed about 123° Tw. it ordinarily contains only minute quantities of dissolved nitrous fumes or none at all, and the same remark applies to the drip in this chamber; if any considerable quantity is observed and the gravity is high, the admission of more steam is requisite, and probably the nitre supply may be diminished slightly without injury to the yield. The bottom acid and drips in the subsequent chambers generally contain increasing amounts of dissolved nitrous fumes the nearer to the exit the sample is taken; but the acid becomes largely denitrated by the action of the sulphur dioxide in the gases as it flows back to the first chamber. In many works the indications obtained by examining the acid made and the colour of the gases &c. are further controlled by thermometer indications and particularly by periodical analyses of the exit gases as regards the percentage of oxygen contained (*vide* p. 734 *et seq.*); preferably by drawing an average sample by means of an aspirator during several hours (24 or less). The regular examination of exit gases in this way was strongly advocated by Mactear in 1877 (C. N. 36, 49, also Jour. Soc. Arts, 26, 554); the results detailed as to the diminution of loss by defective conversion of sulphur dioxide into vitriol effected by means of the control afforded by the frequent periodical determination of this average amount of sulphur compounds in the gases have, since then, led to this method being largely adopted; according to Lunge, however, 'factories thus controlled do not obtain any better yield of sulphate than other well-managed works. Some contend that they have greatly lessened their losses by that control; but that only proves their former management to have been faulty' (Sulphuric Acid and Alkali Manufacture, p. 574).

The temperatures possessed by the gases throughout a series of chambers always show a gradual diminution from the point where the burner gases enter inwards, excepting in so far as local increments in temperature are brought about by the introduction of steam jets; for although the reactions culminating in the oxidation of SO_2 to sulphuric acid as a whole evolve heat, yet the enormous surface exposed by the chambers brings about so much cooling by convection and radiation as to more than counterbalance the heat generation inside. For a constant external atmospheric temperature, and a constant supply of gases at a given temperature and of a given composition, the rate of formation of vitriol in each chamber will be constant, and so also will be the radiation and convection cooling effect; consequently, a constant average excess of temperature of the gases inside over that of the atmosphere will be attained in the case of any given chamber when the amount of heat developed inside is just equal to the atmospheric cooling effect in a given time; and this excess of temperature will be proportional to the heat development—*i.e.* to the amount of vitriol formed in that chamber. For a series of equal-sized chambers, therefore, the excess temperatures of the gases inside as compared with the external air will form a decreasing geometrical series, just as the amounts of vitriol formed in each chamber respectively. In actual practice, however, figures exactly illustrating this are never observed, inasmuch as none of the necessary conditions are ever constant enough to bring about absolute thermal equilibrium, more especially the temperature of the external air. Still, the gradation is sufficiently well marked to render the relative indications of a set of thermometers applied to the various chambers a valuable guide as to regularity of working. This system of checking the work is more used on the Continent, especially in Germany, than in Britain; naturally the thermometer indications are far more reliable if the chambers are enclosed by boarding &c. so as to diminish the variable effect of atmospheric cooling (which, according to Eschellmann, may produce a difference of some 5° between the hottest and coolest parts of the 24 hours) and changes of weather and season. Moreover, different parts of the same chamber will necessarily show different temperatures,[1] the upper part being a little warmer than the bottom and the exit end cooler than the entrance. In the first chamber of the series it is usual so to arrange matters that the gases enter at from 60–70°C.; if a higher temperature is maintained much increase in the rate of wear by corrosion is apt to be brought about. With Glover towers this is rarely the the case, but without them it is often apt to occur. From the exhaust chamber the exit gases emerge at a temperature varying with the season of the year and the steam supply; in cold weather only a few degrees above freezing point, in summer 25–40°C. are not infrequent limits. The *average* temperature of the whole series is always higher in summer than in winter, so much so that if the chambers are working to their full capacity in the colder season, either a notable increment must be made in nitre consumption in hot weather, or else a distinct decrement in yield is observed on account of the larger volume occupied by the gases, unless the rate of production is proportionately lessened to avoid these sources of increased cost.[1] There appears also to be some reason for supposing that the higher the temperature of the chambers the greater is the amount of destruction of available oxides of nitrogen by the secondary actions giving rise to nitrous oxide and nitrogen; so that there is a general consensus of opinion that about 50°C. is the most advantageous average temperature, the earlier chambers being somewhat hotter, and the later ones cooler, than this.[2] In the French system of 'forced' work ('production intense,' p. 737), the temperatures of each successive chamber in the series are something like 20° above those that would be observed when working under the ordinary conditions.

In the case of brimstone chambers working on a comparatively small scale, the effects of climatic varieties are proportionately more marked than with larger pyrites chambers. In cold climates the temperature sometimes becomes so much lowered in winter as to fall considerably below that requisite for best working; so that instead of less nitre being required than in summer, a *larger* proportion is required to compensate for the diminished activity due to lower temperature. Covering the chambers in by inclosing them in shedding is obviously the simplest remedy, whilst cooling pipes are unnecessary; or if provided for summer use they should in winter be swathed in non-conducting coatings.

The pressures obtaining throughout a series of chambers are not absolutely uniform. The hot burner gases are lighter bulk for bulk than ordinary cool atmospheric air, and consequently tend to ascend upward, and produce an indraught at the burners; the suction of the chimney (or, when a chimney is not employed, that of a steam jet) attached to the far end similarly tends to draw air in, as also does the diminution in volume due to cooling and condensation of gases to liquid vitriol. Notwithstanding, there is generally a slight excess of pressure in the first chamber, so that on opening a testing-hole gases tend rather to issue outwards than air to enter. In the second chamber of a series the same result is usually faintly noticeable, although here there is almost equilibrium. Near the exit from the last chamber a tolerably marked indraught is noticeable on opening a plug. In order to determine accurately the pressures at any given points, and to measure the speed of the gas currents passing through the tunnels &c., various forms of manometer and anemometer are in use. Of the latter, Fletcher's and Swan's are those mainly used in Great Britain. Opening a damper between the burners and chambers tends to increase the average pressure in the latter, whilst opening one between the last chamber and the final exit tends to reduce it.

In well-conducted works the amount of draught is usually so regulated that sufficient surplus air is drawn in at the burners &c. to give an average excess of oxygen over that consumed in the chambers amounting to 5–6 p.c. in the exit gases (*v.* p. 737).

In order to draw off acid from the saucer of the chamber without employing a cock (always liable to get out of order and leak) a small leaden cistern is arranged level with the saucer, and provided with a pipe leading away the acid to wherever it is required. A siphon, with loose leaden buckets over the ends so as to keep it full when not in use, is then dipped, one leg into the saucer (made to project in the form of a corresponding cistern), and the other into the pipe cistern, when a flow of acid is brought about for as long a time as may be requisite. Fig. 7 represents a more complex arrangement, working on the same principle, the siphon being set in action by lowering the counterpoised reservoir *d*; a simpler arrangement is often used, where the siphon is superseded by a plug with a handle attached.

Widely different views have been held by different experimenters as to the relative functions of different parts of the same chamber—*i.e.* the lower, middle, and upper zones, and the portions adjoining the sides and roof, as compared with the interior. At one time the sides and roof were regarded as the active portions, liquid acid condensing thereon as fluid condenses from vapour in distillation upon the sides of the cooling worm; and it was supposed that by increasing the surface on which the gases could impinge a larger amount of work would be done in a given cubical space. Later experience, however, has shown that if the extra condensing surface is obtained by employing such a shaped chamber that the side and roof bear a large proportion to the cubic contents, the rate of cooling is more rapid but the gain in rapidity of make is not very marked; whilst if it is obtained by filling up the interior of the chamber with coke, horizontal layers of sheets of glass an inch or two apart (Ward's patent), or other condensing surfaces, the interference with the draught and the practical difficulties introduced more than outweigh the advantage gained by the surface action of the solids introduced; so that chambers thus packed have never come into general use excepting in the form of coke towers attached to the exit end of chambers not provided with Gay-Lussac columns, whereby a notable amount of vitriol is filtered out, so to speak, from the waste gases by intercepting the floating vesicles and spray that have not completely subsided in the chambers. The action of solid surfaces *inside* the chamber appears, in fact, to be much more that of mechanically collecting together the liquid vesicles floating about than of facilitating the chemical changes going on in the way that platinum asbestos acts in the production of sulphuric anhydride. The total action, however, under favourable circumstances is very marked: thus Mactear obtained the following results with a series of trays, each 1 foot square, placed in a chamber (*a*) alone; (*b*) with twelve glass sheets, 1 foot by 6 inches, placed vertically in the tray, 1 inch apart; (*c*) the same sheets placed horizontally 1 inch apart (S. C. I. 1884, 228).

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[1] Lunge states that at the Aussig works the average summer chamber temperature is 12·5°C. higher than the winter one. In all factories known to him, less nitre is requisite in the cooler season, and irregularities in working are then less frequent; if everything else remained the same a diminution of some 3 p.c. in the yield is observable in summer as compared with winter. Payen states that whilst 55° to 60° is a normal temperature in winter, 65° to 80°, or some 20° higher, is observed in summer.

[2] H. A. Smith regarded 93°C. as the proper temperature for making vitriol, attained only in the part of the chamber where the action goes on most rapidly; but few, if any, practical vitriol-makers endorse his views on this point.

(*a*) Acid collected in trays alone .	100
(*b*) Acid collected in trays with vertical glass plates . . .	231
(*c*) Acid collected in trays with horizontal glass plates . . .	455

With the last form of arrangement there was obviously less interference with air currents, so that a maximum of gases laden with vesicles impinged on the glass surfaces and deposited the floating vesicles in consequence. In similar fashion flat surfaces were disposed in the chambers vertically in a plane at right angles to the main current of gases, so that the front side received a larger proportion of impinging vesicles, gutters being attached so that the acid deposited at both front and lee sides could be collected separately. It was found that the proportions were respectively as follows:

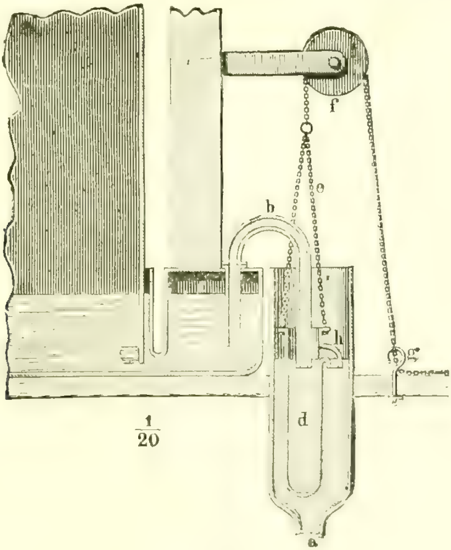

FIG. 7.

Front side	100
Lee side . . .	78
Total . . .	178

whilst 175 parts were collected from both sides jointly of a similar plate arranged edgeways towards the current instead of at right angles thereto.

A set of similar vertical plates arranged at different levels (5 feet 3 inches, 10 feet, and 14 feet 6 inches, above the floor of a chamber 18 feet high) gave the following results: (*a*) when protected by a cover from receiving drippings from the roof of the chamber; (*b*) when unprotected:

	Protected	Unprotected
High . . .	100	100
Middle . .	111	114
Low . . .	146	165

The lowest plate always gave the largest collection, as might be anticipated, since by gravitation and coalescence more and larger vesicles would naturally exist at a lower level, and therefore more total acid would impinge at a given time at that level. Precisely the same result was found on analysing samples of the atmosphere inside the chamber at various levels; the amount of sulphur dioxide in a given volume of gas lessened from the top downwards, whilst the quantity of suspended vitriol vesicles increased, as might be anticipated, since the entering gases, being warmer, tend to rise immediately to the top, and lose a portion of the SO_2 present by conversion into vitriol vesicles before they descend again to the lower levels.

	[illegible]	
	[illegible] of SO_2	[illegible] of H_2SO_4
Top zone . .	100	100
Middle zone. .	89	124
Lowest zone .	86	157

It hence results that most chemical action takes place in a given space at the top of the chamber and least at the bottom, for precisely the same reason that more takes place in the first chamber of a series than in the second, and more in that than in the third, and so on. Exactly the opposite conclusion was arrived at by H. A. Smith, whose experiments on the subject, however, hardly warrant his deductions therefrom.

Lunge and Naef (S. C. I. 1884, 633), on the other hand, deduced from their experiments that the gases in the central part of a chamber contain a higher proportion of sulphur than those at top, bottom, or sides, indicating a smaller formation of vitriol in the central region; whilst Hasenclever concluded that the formation of vitriol is practically the same per given amount of space in all parts of the interior of a given chamber. Along the roof and sides, however, a larger collection of liquid is necessarily brought about on account of the cooling influence of the external air, whereby true condensation of aqueous vapour is effected as well as mechanical reception of floating vesicles; whence it results that the 'drip' collected from a gutter along the sides always shows a lower density than that from a tell-tale in the interior.

If the amount of chemical action going on in a given space be most in the top zone, obviously the temperature must be greater there than at a lower level (excepting in the immediate proximity of the roof or sides, where aerial cooling goes on); this, in fact, is always found to be the case, unless local causes set up air currents interfering with the normal result. The difference of temperature is variable with the size and shape of chamber and general conditions, but usually does not exceed a few degrees; from 4° to 5°C. were observed by Lunge and Naef in a series of investigations carried out with a set of three chambers at Uetikon (*l.c. supra*). A perceptible increase in the rate of chemical reaction was noticed in the vicinity of the walls, apparently due to their surface action. It was also observed that whilst the majority of the sulphuric acid made was formed in the first half of the first chamber, the portion converted in the first half of the second chamber was greater than that in the second half of the first chamber, instead of less, as would naturally be expected, the intimate commingling effected by passing through the connecting tunnel being apparently the cause of this seeming irregularity; from which it may perhaps be inferred that a long series of comparatively small chambers is likely to be a more effective disposition of chamber-space than a shorter series of longer ones possessing the same aggregate cubic capacity, on account of the larger number of comminglings to which the gases are subjected in the connecting tunnels.

Naef (Chem. Ind. 1885, 285) and A. Schertel (Chem. Ind. 1889, 80) confirm these results as regards the much greater rate of formation of vitriol in the first half of a chamber as compared with the second half, and the increased rate effected in passing from this second half to another chamber. Schertel attributes this simply to the introduction of fresh steam along with the gases into the second chamber, whereby nitrosulphonic acid is decomposed more rapidly and nitrous acid liberated.[1] In the course of his experiments it was shown that a multiplication of solid surface within the chamber, such as dividing partitions, as previously pointed out by Ward and others (*supra*), is of advantage in hastening the formation of vitriol. Lunge and Horstmann regard this advantage as due to the bringing together of vesicles of comparatively strong nitrosulphonic acid and of water or dilute sulphuric acid, so as to cause them to react on one another more rapidly, thus liberating active nitrogen oxides. To facilitate this they sug-

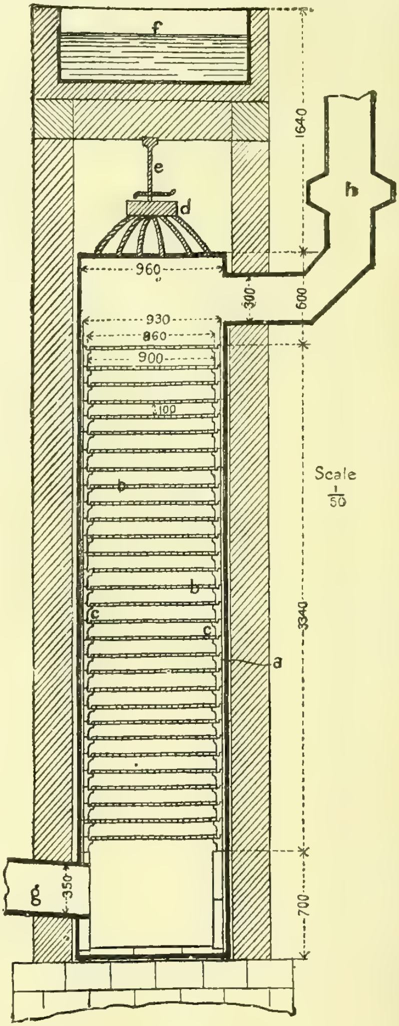

Fig. 8.

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[1] According to the view put forth by the author (p. 727 *et seq.*) that the main reactions occurring in the vitriol chamber (whatever their actual nature) take place *on the surface of the vesicles of condensed steam*, gradually converting them into vesicles of dilute sulphuric acid, it is obvious that an enhanced activity must necessarily accompany the introduction of a fresh quantity of vesicles by blowing in more steam.

gest (Zeit. f. Angew. Chem. 1889, 385; also S. C. I. 1889, 774) the use of 'Plattenthürme' or plate columns, consisting of columns of perforated porcelain plates, *b b* (fig. 8), contained in a lead-lined tower or vertical tube, into which the gases enter at *g*, emerging at *h*; water or dilute acid is led in from a reservoir at the top *f* by the distributing pipes *e*, *d*. Each plate is separately supported by bearers, *c c*, in such a way that in case of necessity any one plate can be removed without disturbing the others. Fig. 9 represents the plates in section, also the disposition in two consecutive rows, and fig. 10 the plates in plan; each plate is covered with a network of small ledges, *d d*, forming squares, in the centre of each of which is a perforation, *e e*, with somewhat raised margin, not reaching up quite so high as the ledges; hence the squares always contain a layer of liquid which overflows through the perforation drop by drop. The plates in two consecutive layers are not identical in shape, differing in the position of the holes, the perforations in the plate above being vertically over the points of union of the ledges on the plate below (fig. 11), so that liquid dropping from the upper plate cannot drop straight through the holes in the lower plates, but strikes the solid portion of the next plate, and is thus scattered about and divided amongst the adjoining squares. The thin layer of liquid resting on the plates and clinging to the holes is thus constantly renewed; whilst the gases and vapours rising within the column are continually being divided into comparatively fine jets by passing through the various orifices, and then striking upon the solid parts of the plates above. The direction of the air current is thus constantly changing, whilst the surface of the liquid is continually being renewed, and thus the most favourable conditions are produced for the mutual action of the gaseous and liquid substances. Moreover, no false channels can exist through which gases or liquid could pass separately without coming into proper contact with one another. These circumstances give the plate column an enormous superiority over a coke-packed tower as an absorbing apparatus. According to Lunge, from 10 to 20 times as much work can be done in the same cubic space. Further, the chemical action of coke on oxides of nitrogen is eliminated. The heat of reaction in the formation of chamber acid furnishes enough heat to evaporate 100 parts of water at 100°C., during the production of 98 parts of H_2SO_4, a quantity some 25 p.c. in excess of the requirements of the process; taking into account losses by radiation &c., this should suffice for a nearly self-contained equilibrium. An ideal disposition would be the following:—Glover tower; small chamber 16 × 16 × 40 feet; one or more plate columns, 3 feet diameter and 13 to 20 high, containing 25 to 40 plates; second chamber and set of plate columns; end chamber for drying the gases; Gay-Lussac tower, to which function the plate column is well adapted.

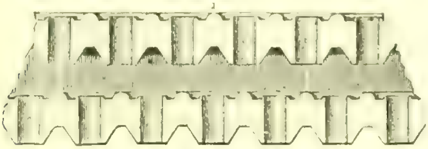

FIG. 9.

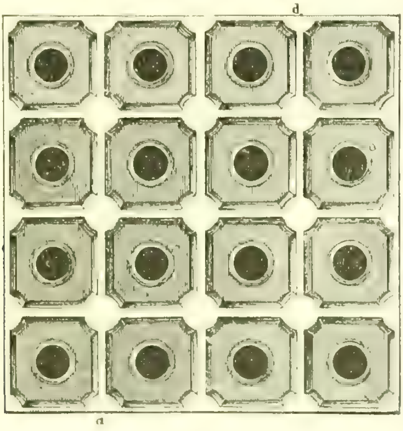

FIG. 10.

Very satisfactory results have attended the introduction of plate columns in the vitriol series after this fashion; thus in one works in Bohemia the placing a column of 16 layers of plates between the first and second chambers of a set of two at once permitted 30 p.c. more pyrites to be burnt; the yield of acid remained the same, whilst the nitre consumption was actually lessened. No acid whatever was made in the second chamber, the use of which might have been dispensed with altogether, excepting for the purpose of cooling and drying the gases before passing into the Gay-Lussac tower. Hence it would seem that the working capacity of the first chamber was really increased by 70 p.c. by the addition of the column (Lunge, 'Sulphuric Acid,' 2nd edition, 1891, p. 990).

Sorel (Bull. Soc. Ind. Mulhouse, 1889, 240; also S. C. I. 1890, 175) traces the increased effect on passing into the second chamber to the reduction of temperature brought about on passing through the connecting tunnel or pipe, the gases being thereby cooled 20° or 30°. Condensation of water takes place, which dilutes the acid in suspension, and suddenly liberates a large quantity of nitrous acid, which thereupon produces a more rapid oxidation of the sulphurous acid.[1] He deduces from his experiments the general result that variations of temperature play a preponderating part in the formation of sulphuric acid; during the movements of the gases, the particles of liquid in suspension pass into zones of different temperatures, with the result of changing their state of concentration of richness in nitrous products, whilst bringing themselves into equilibrium with that part of the gaseous atmosphere that surrounds them. 'Therein lies the secret of the rationale of the sulphuric acid process.' Although the normal effect of the walls of a chamber is to bring about a cooling action by radiation, yet, according to Sorel's observations, this cooling influence is only felt close to the wall, and in certain cases the temperature at the side of the chamber a few inches inwards is notably higher than the interior temperature at the axis. He agrees with Abraham (D. P. J. 245, 414) that each molecule travels in a spiral round a horizontal axis from one extremity of the chamber to the other, a view regarded by Lunge as altogether compatible with his own experiments. As the result of his observations, he suggests the following order of apparatus:—A Glover tower in which 25 p.c. of the total yield is produced, a chamber capable of oxidising 75 p.c. of the sulphurous acid that enters it (Lunge and Naef's results expressed diagrammatically show that this chamber would have about one-quarter the capacity of ordinary chambers); following upon this chamber, a series of cooling pipes and small towers, the latter traversed by acid of 60°B. from top to bottom, whilst the gases and steam are introduced at the bottom. Assuming that these towers have each a cubical content equal to half that of the Glover tower, with three towers there would be produced upwards of 93 p.c. of the total theoretical yield, with a saving of about 60 p.c. in the capacity of the apparatus used. At the date of writing, however, it does not appear that these arrangements have been submitted to the test of practical experience.

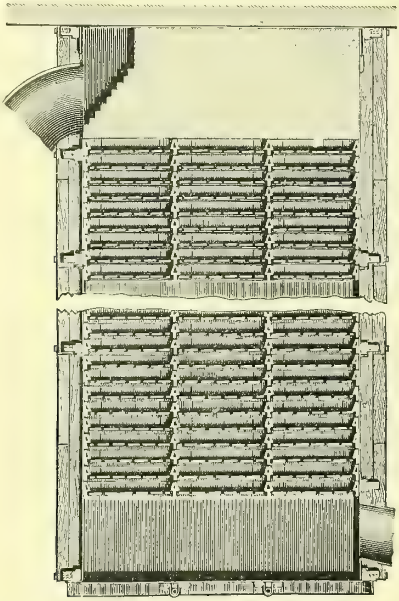

Fig. 11.

In discussing the advances made in sulphuric acid manufacture up to the end of 1891, Hasenclever states (Chem. Ind. 1892, 15, 69) that, as it is now recognised that the reactions taking place in a vitriol chamber can be promoted by bringing about a more intimate contact of the gases, in various works a system is being adopted whereby several small chambers connected by comparatively narrow tunnels are provided at the exit end; the gases are thereby intimately commingled and the final stages of the manufacture considerably hastened. At Petrowitz in Austria, and Ghent in Belgium, lead chambers in the form of gasometers have been introduced; but as yet nothing has been published to show that they possess any special advantages.

E. and T. Deplace have patented (S. C. I. 1891, 254) a peculiar form of vitriol-making plant, consisting of modified pyrites kilns, two Glover towers (one to cool the gases and concentrate the liquors, the other to denitrify the

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[1] Inasmuch as the cooling would tend to the precipitation of *liquid water vesicles as mist*, which would not coalesce instantaneously with the acid vesicles, it would seem probable that the increased rate of action is due as much *to the increased amount of water surface* thus brought into play, as to the evolution of nitrous acid.

Gay-Lussac nitrous vitriol), a circular or polygonal chamber of annular plan, into which the gases are led by two inlets, one near the circumference and one towards the central part of the annulus; a second annular chamber concentric within the first, and finally a Gay-Lussac tower. The leading idea is constantly to change the direction in which the gases are travelling, and so insure more thorough mixing and quicker interaction. Lunge considers that, apart from the extra cost of construction, the advantage derived from the more complete mixing of the gases is more than counterbalanced by the lessened cooling effect of the inner wall.

9. **Gay-Lussac and Glover towers.** Although the use of these subsidiary appliances is by no means universal, yet the advantages gained by the employment of the two together under proper conditions are so great that they are now adopted in almost all works where anything like scientific management is in vogue. The Gay-Lussac tower, as originally constructed, was simply a scrubber, down which tolerably concentrated vitriol was passed (of about sp.gr. 1·7 to 1·75); this absorbed the nitrous fumes from the exit gases passing up the tower, with the formation of nitric acid and nitrosulphonic acid, $SO_2(OH)(NO_2)$; the oxides of nitrogen were then recovered by blowing steam into the nitrous vitriol,[1] or by passing it through a 'denitrificator,' consisting of another scrubber, into which part of the burner gas and a jet of steam were introduced, so that the diluting action of the steam and heat in decomposing nitrosulphonic acid in accordance with the reaction $2SO_2(OH)(NO_2) + H_2O = 2SO_2(OH)_2 + N_2O_3$ was further aided by the chemical action of the sulphur dioxide on the nitric acid.[2] Various practical difficulties prevented the general adoption of Gay-Lussac's process for more than thirty years; although it was invented in 1827, it was employed by very few (and, after trial, in many cases was abandoned), it being considered that the cost of re-concentrating the diluted vitriol run out from the denitrificator, the liability of the apparatus to get out of order and become injured by corrosion, the inconvenience of having to pump up concentrated acid to the top of the scrubber, and such like matters, more than outweighed the value of the nitre undoubtedly saved by its use. As the amount of scientific skill necessarily bestowed on the manufacture (through increasing competition and other causes) became greater, the reverse opinion began to gain ground; and when about 1860, and during the next few years, the use of Glover towers became general for utilising the waste heat from the burners for concentrating and denitrating the chamber acid, and thus cooling the gases without requiring any chilling appliances, it soon became obvious that by simply mixing the nitrous vitriol from the Gay-Lussac tower with the chamber acid and passing the mixture through the Glover tower, the nitrous gases contained in both could be recovered at a minimum of cost, inasmuch as the concentrated acid obtained at the base of the Glover tower was strong enough for use as absorbent in the Gay-Lussac scrubbers without any further evaporation being requisite. At first objections were raised to this mode of procedure, it being considered that considerable loss of nitrous fumes would be incurred through reduction to nitrous oxide or nitrogen taking place at the higher prevailing temperature; but experience has shown that these fears were practically groundless, since the great bulk of the nitrous fumes are liberated at the upper part of the Glover tower when the temperature is lowest; and that consequently by the use of the two towers combined a reduction can be effected in the amount of nitre consumed to the extent of 60 to 70 p.c., not only without any detriment to the process, but with the positive advantages of enabling more acid to be made in a given amount of chamber-space, and diminishing considerably the quantity of sulphur dioxide ultimately escaping unchanged—*i.e.* increasing the yield from a given amount of material; these results being brought about in consequence of the larger proportion of nitrous gases present in the chamber atmosphere at any given moment, owing to the increment due to the cumulative effect of the Gay-Lussac tower exceeding the diminution due to the decreased nitre consumption.

To effect this result the cubic capacity of the Gay-Lussac tower must not be too small in proportion to that of the set of chambers to which it is attached, and the absorbing sulphuric acid must be neither too low in strength nor deficient in quantity. As regards the relationship between capacity of tower and chambers, taking the latter as holding 1,000 volumes, the former is frequently so constructed as to contain 10 to 12·5 volumes (reckoning only the leaden shell, and making no allowance for lining or coke packing); but somewhat larger amounts are preferable, 12·5 to 15 or even 20; larger amounts still, up to 30 or 35 per mille, are essential when the system of 'forced' working ('production intense') is adopted, as in some French works (p. 737). Thus a pair of towers, each 6 feet square (internally) and 40 high, would jointly hold 2,880 cubic feet, and if connected with a set of chambers of capacity 150,000 cubic feet would give a ratio of $\frac{2,880}{150,000} = 19{\cdot}2$ per mille; whilst a single tower, 7 feet square and 50 high, would hold 2,450 cubic feet, and when applied to a set of chambers of capacity 200,000 cubic feet would give the ratio $\frac{2,450}{200,000} = 12{\cdot}25$ per mille. If the capacity of the tower be *m* per mille relatively to that of the chambers, and if the rate of working be such that the gases supplied are sufficient to refill the chambers n times in 24 hours, obviously the tower will be refilled $1{,}000 \times \frac{n}{m}$ times daily, or once in

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[1] As late as 1890 this method was still in use at Freiberg, on account of the low temperature at which the gases enter the chamber, because of the special arsenic-condensing arrangements (Lunge, 'Sulphuric Acid,' 2nd edition, 1891, p. 570).

[2] According to Lunge's observations, nitrous vitriol obtained in the Gay-Lussac tower does not contain any nitric acid, the older analyses leading to that conclusion being incorrect. If nitrogen tetroxide be present in the gases, it should form nitric acid by the reaction (occurring in glass vessels) $H_2SO_4 + N_2O_4 = SO_2(OH)(NO_2) + HNO_3$; but the reducing action of the coke causes nitrosulphonic acid to be formed instead by a reaction which may be written $2H_2SO_4 + N_2O_4 = 2SO_2(OH)(NO_2) + H_2O + O$, the oxygen being taken up by the coke (S. C. I. 1885, 31). At 20°C. this action is languid, but at 38°–40° it is much more rapid. Under certain conditions, this reducing action of coke may lead to the formation of NO from higher oxides, which may pass away unabsorbed.

$$\frac{24 \times 60}{1{,}000 \times \frac{n}{m}} = 1{\cdot}44 \times \frac{m}{n}$$

minutes; or once in $86{\cdot}4 \times \frac{m}{n}$ seconds; so that if the height of the tower be h feet, the average velocity of the gases passing through the tower (reckoned as *empty*, not taking into account the coke packing) will be $\frac{hn}{86{\cdot}4 \times m}$ feet per second. In order to obtain good absorption with a supply of acid at about 150°Tw. in quantity equal to 67 to 100 p.c. of the daily make, the value of the velocity thus calculated should not exceed at the most ·5 feet per second, but better results are obtained with a velocity of $\frac{1}{2}$ to $\frac{2}{3}$ this limit—*i.e.* of ·25 to ·33 feet, or 3 to 4 inches per second; thus in the two instances just quoted the values are $\frac{40 \times 9}{86{\cdot}4 \times 19{\cdot}2}$ and $\frac{50 \times 9}{86{\cdot}4 \times 12{\cdot}25}$ or ·27 and ·34 feet per second respectively if it be supposed that $n = 9$, *i.e.* that the chambers are refilled 9 times daily. Of course the actual mean velocity of the gases through the interstices of the packing is much greater than this amount, in proportion as the capacity of the empty tower exceeds that of the interstitial space.

Towers of more than 6, or at most 7, feet square in section were till recently rarely employed, on account of the supposed increased difficulty in maintaining a regular equable flow of acid down all parts alike; but of late years much wider towers have been used, up to 12 or 14 feet, without any drawbacks being noticed due to increased width (Lunge). If the height much exceeds 40–50 feet, there is considerably increased difficulty in pumping up the acid, whilst the weight of the superincumbent layers of packing tends to crush the lower layers and block the interstices; so that if the bulk of gases to be dealt with is such as to require larger tower capacity than can be well afforded by one column, two or more (preferably worked so that the gases do not traverse each in succession, but pass equally through all) answer better than one larger. When two towers in succession are employed, the gases passing out at the top of the first are brought down again to the bottom of the second by a pipe, and not made to *descend* through the second; otherwise, but little absorption is effected, as when the gas and acid travel in the same direction their mutual action is very languid. In order to diminish the work required of the tower, it has been proposed to wash the gases previously by making them pass through a preliminary tower not packed with coke throughout, but furnished with an arrangement for producing a copious shower of rain of sulphuric acid (S. C. I. 1885, 456). According to Lunge, this method does not work very satisfactorily in practice, probably because the drops of acid fall too rapidly to enable them to act upon the gases efficiently.

Gay-Lussac towers are usually constructed of sheet-lead supported by wooden scaffolding in the same fashion as the chambers (figs. 12 and 13);[1] some manufacturers use much stouter lead than for the chambers, 10 to 14 lbs. per square foot, whilst others employ 6 or 7 lb. lead only. A firebrick lining is sometimes used for the lower portions, to prevent the thrust on the lead from the weight of the packing. Square sectioned towers are usually preferred, as involving somewhat less trouble in construction; but circular ones have the double advantage of giving more cubic space for a given area of sheet lead employed and being more readily fed regularly and equally in all parts with the absorbing acid. Hard-burnt coke is usually employed as packing, but various other materials have been used, such as fragments of glass and porcelain, or such like substances capable of resisting the action of the acid. These have the disadvantage of possessing a less irregular contour than coke, and, therefore, exposing less active surface; but, on the other hand, they are without chemical action on the higher oxides of nitrogen, whereas coke partially reduces them to NO, to an extent dependent on the temperature—very slightly at ordinary temperatures, but much more quickly at 30–40°C. (Lunge). Moreover, coke is much more apt to

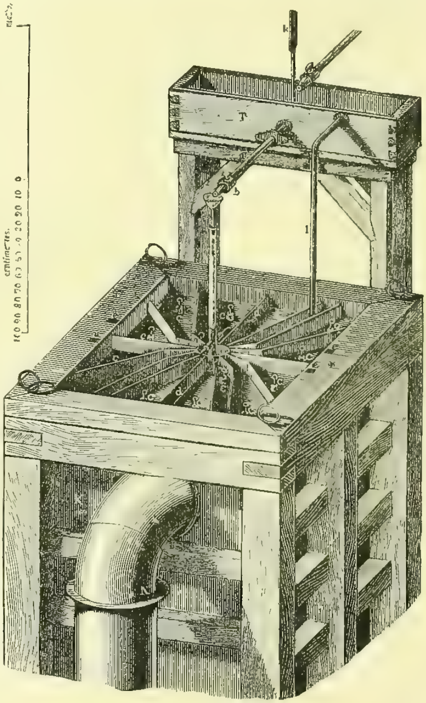

Fig. 12.

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[1] In the South of France octagonal Gay-Lussac towers are in use built of volvic lava, like a hydrochloric acid condenser, without any lead shell (Lunge).

become disintegrated and break up into small fragments, which block up the interstices and impede the draught. The perforated stoneware plates used for 'plate columns' (p. 749) answer well, as they bring about a most thorough washing of the gases. When coke packing is employed, the lamps are carefully laid piece by piece in regular layers upon a series of parallel rows of firebrick, supporting transverse tiles placed a little apart so as to form a kind of grating underneath which the gases enter; usually the base is packed with large fragments, the middle with somewhat smaller ones, and the top with lesser lumps about the size of large potatoes or apples. On the top of the tower is a leaden basin divided into compartments, with perforations in the base of each, so distributed over the total sectional area that when the various compartments are kept equally supplied with acid by a rotating distributor working on the principle of the well-known reaction machine 'Barker's mill' (or in any other convenient way[1]), an equable shower of acid drops falls on the coke at the top over its surface, so that the descending acid flows as far as possible equally through all portions of the mass of packing. The denitrified gases either escape directly into the air at the top of the tower, or are brought down by a descending flue connected with the chimney of the works to create draught through the chambers, regulated as required by a damper. Glass panes, or 'sights,' are fixed in the supply and exit flues, so that the colour of the entering and denitrified gases can be inspected and compared; the former should be markedly ruddy, the latter practically colourless, and incapable of generating red fumes on admixture of air, indicating absence of nitric oxide. The acid employed is usually of sp.gr. 1·725 to 1·775 (145°-155° Tw.), and is forced up to a supply cistern at the top of the tower by means of compressed air injected into a vessel contain-

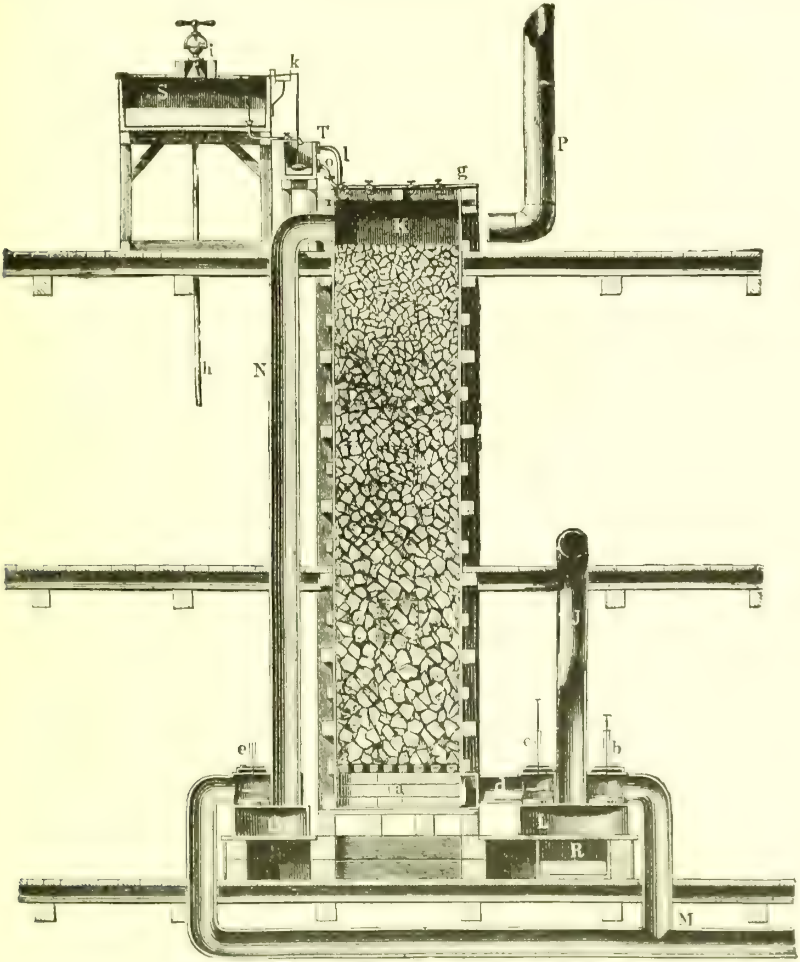

FIG. 13.

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[1] For det[illegible] see, e.g. Lunge, [illegible]

ing the acid, and provided with a tube passing down internally to near the base, the action being that of a 'wash-bottle,' or somewhat like that of an ordinary soda-water siphon.

In comparatively small works, *e.g.* brimstone acid factories, a sufficiently effective arrangement for absorbing nitrous fumes is sometimes employed, consisting of a number of stoneware pipe columns, filled with coke, fed at the top with strong acid from an acid main, and all communicating below with a reservoir on which they stand, from which the nitrous vitriol is drawn off by a pipe. Earthenware cylinders filled with layers of tiles and dishes one above another are sometimes used, or a series of Wolfe's bottles.

The quantity of nitrosulphonic acid contained in the liquid running out at the base of the tower depends on the proportion of acid used in the tower and on the total quantity of oxides of nitrogen in circulation; usually such a quantity of acid is employed that the nitrous vitriol contains nitrogen compounds equivalent to 1 to 2 p.c. or more of N_2O_3, which generally entails the passing through the tower daily of an amount of acid equal to from three-quarters to once and a quarter times the daily production. The stronger the acid used, naturally the more powerful is its action in absorbing nitrous fumes, and the less may be employed; acid weaker than 140°Tw. (sp.gr. 1·70) is almost unserviceable. Admitting that the acid passed through the tower is equal to the daily production, and has a strength of 150°Tw.—*i.e.* contains about 81 p.c. H_2SO_4 corresponding with 26·4 p.c. of sulphur—and that it absorbs an average amount of nitrous fumes equivalent to only 1 p.c. of N_2O_3 or 2·24 p.c. of $NaNO_3$ (or, what comes to the same thing, that the acid passed through the tower is two-thirds of the daily production, and contains 1·5 p.c. of N_2O_3, or that it is once and a half times the daily make, and contains ·67 p.c. of N_2O_3), it results that 100 parts of sulphur burnt correspond with $100 \times \frac{2{\cdot}24}{26{\cdot}4} = 8{\cdot}5$ parts of nitre equivalent to the nitrous fumes absorbed; so that if 4 parts be also used in the nitre-pots, the total amount in circulation will be equivalent to 12·5 parts of nitre per 100 of sulphur burnt. This is probably considerably below the amount actually in circulation in most cases, as, according to analyses of nitrous vitriol published by Winckler, Kolb, Lunge, and others, the quantity of oxides of nitrogen present calculated as N_2O_3 is from 2 to 4 p.c. H. Pemberton (S. C. I., 1883, 414) found in a brimstone chamber that the nitre used *as such* was 3·5 parts per 100 of sulphur burnt, whilst that derived from the nitrous vitriol was 12·1 parts, giving a total of 15·6; and Hurter has similarly found 19·6 as the total circulating in a pyrites chamber. On the whole, it appears to be clearly proved that the well-known effect of Gay-Lussac and Glover towers in diminishing the amount of chamber-space required to make a given quantity of vitriol, even when less nitre is allowed, is due to the fact that by the accumulative effect of the regeneration of nitrogen oxides a much larger amount of these bodies is present in the chambers relatively to the sulphur dioxide than is the case when no towers are used, even though the nitre is then as much as 10 parts per 100 of sulphur burnt, instead of only 3 to 4 parts. In some Continental works it has been the practice of late years to make frequent tests of the nitrous vitriol supplied to the Glover tower, so that an estimate may be formed of the total amount of available oxides of nitrogen entering the chamber as compared with the sulphur burnt, including that from the nitre (or nitric acid) used. Lunge states that when 24 cubic feet per pound of sulphur is allowed, this total (expressed as nitre) may be allowed to fall as low as about 10 parts of 96 p.c. nitre per 100 of sulphur burnt; but with smaller amounts of chamber-space, from 15 to 20 parts of 'total nitre' is put through the system, proportionately larger nitre-recovery apparatus being then requisite. In the French 'forced' system ('production intense,' p. 737), the 'total nitre' in circulation reaches as high as 25 parts per 100 of sulphur burnt; in this case the quantity of acid passed through the tower daily amounts to *at least* twice the daily make.

According to Benker and Lasne, when sulphur dioxide is practically absent from the gases passing from the exhaust chamber to the Gay-Lussac tower, the ruddy fumes of available nitrogen oxides contain much N_2O_4, which more or less escapes condensation in the tower. To avoid this loss, they have taken out a German patent (17,154, Feb. 1881) for the introduction at the base of the tower of a stream of burner gases mixed with steam in such quantity as to cause the reduction of N_2O_4 to N_2O_3, which is then completely absorbed, forming nitrosulphonic acid thus:

$$2H_2SO_4 + N_2O_3 = 2SO_2(OH)(NO_2) + H_2O.$$

Lunge regards (B. 15, p. 488) their views on the subject as wholly incorrect, N_2O_4 being, according to him, readily soluble in sulphuric acid with the formation of nitrosulphonic and nitric acids, thus—

$$N_2O_4 + SO_4H_2 = SO_2(OH)(NO_2) + NO_3H$$

The advantages alleged to be gained by the introduction of sulphur dioxide he considers do not exist when the chamber process is properly attended to, although in case of faulty working they may be attained, as in that case the tower serves to carry on further the chamber process; but they are counterbalanced by the great danger introduced of denitrating again the nitrous vitriol formed in the upper part of the tower—especially at night, when the superintendence is less rigid—and so causing ultimately loss of nitrous fumes rather than any gain by increased absorption.

As worked in Britain the loss from non-absorption of available oxides of nitrogen in the tower, together with the formation of nitric oxide, generally amounts to about one-fifth, or at most one-fourth, and often only one-sixth, of nitre employed when this is from 3 to 4 parts per 100 of sulphur burnt. Of course, under unfavourable conditions, or through derangements of chamber-working, temporary increments in the escape are from time to time met with; but one-fifth may be taken as a fair working average limit. If the last chamber of a series is unusually strongly coloured, a higher loss from incomplete absorption of soluble oxides is apt to be occasioned; whilst if lighter than usual, an increased loss is also often occasioned, but in this case the cause is formation of insoluble nitric oxide owing to presence of excess of sulphur dioxide.

The examination of the exit gases passing away from the Gay-Lussac tower is a most important part of the control operations requisite for carrying on the work efficiently. Besides the examination of samples drawn off from time to time, it is always desirable to have an average sample drawn every 24 hours by means of any convenient form of aspirator capable of working regularly and uniformly, drawing off a cubic foot per hour, or more, of gases, and recording the volume on a gauge or by a meter. The gases thus aspirated are made to pass through absorption bottles containing caustic soda, whereby the nitrogen and sulphur acids present are retained, so that by the examination of the absorbing fluid the average amounts of these substances carried away in the gases are deduced. Hurter and Lunge ('Alkali Makers' Pocket-book,' p. 86) recommend the following arrangements, agreeing in the main with those published by the British Alkali Makers' Association in 1878. A series of 4 absorbing bottles or tubes is employed, each containing 100 c.c. of fluid, normal pure caustic soda solution (31 grms. Na_2O per litre, in the first three, and distilled water in the fourth, the depth of liquid in each being at least three inches, and the aperture of the inlet tubes not exceeding $\frac{1}{50}$ inch in diameter, measured by a standard wire. The contents of all four bottles being united with as little dilution by washing as possible, the total is divided into three equal parts, of which one is reserved in case of accident, one tested with standard acid to find the 'total acidity,' *i.e.* the amount of alkali neutralised, and the third gradually poured into a warm solution of potassium permanganate strongly acidified with sulphuric acid; a small excess of permanganate must be present, subsequently reduced by a few drops of sulphurous acid solution until only a faint pink tint remains. In this way all the nitrogen oxides are converted into nitric acid, which is then determined by adding to a recently titrated solution of ferrous sulphate (about 25 c.c. of solution containing 100 grms. of crystallised salt and 100 grms. of sulphuric acid per litre), 20-25 c.c. of pure sulphuric acid, and after cooling slowly adding the nitric acid solution; the operation is carried out in a flask through the cork of which pass tubes for removing the air in the flask and replacing it by an atmosphere of carbon dioxide, a current of which is kept up whilst the contents of the flask are heated to boiling; or the flask may be closed by means of a perforated cork, through which passes a piece of glass tube, terminating in a Bunsen caoutchouc valve, permitting egress of steam, but not allowing air to enter (Lunge). After from 15 to 60 minutes the liquid becomes of a clear bright yellow, and the unoxidised ferrous sulphate is determined by a semi-normal permanganate solution (yielding 4 grms. oxygen per litre). If V be the volume of air aspirated after reduction to 0°C. and 760 mm., x the number of c.c. of normal sulphuric acid (49 grms. H_2SO_4 per litre) used for the neutralisation of the excess of alkali in the first titration, y that of permanganate used during the second test, and z the quantity of permanganate equivalent to the iron solution originally employed, then the *total acidity* expressed as SO_3, the *sulphur* S, and the nitrogen N, are respectively given by the formulæ

Grms. per cubic metre

Total acidity . $SO_3 = \frac{0{\cdot}12(100-x)}{V}$

Sulphur . . $S = \frac{0{\cdot}008(600+6x-z+y)}{V}$

Nitrogen . . $N = \frac{0{\cdot}007(z-y)}{V}$

Grains per cubic foot

Total acidity[1] . $SO_3 = \frac{1{\cdot}852(100-x)}{V}$

Sulphur . . $S = \frac{0{\cdot}12346(600+6x-z+y)}{V}$

Nitrogen . . $N = \frac{0{\cdot}10803\ (z-y)}{V}$.

Nitric oxide is estimated by passing the gases that have already passed through the four bottles through an absorption tube containing 30 c.c. of semi-normal permanganate and 1 of sulphuric acid, sp.gr. 1·25. A known quantity of standardised ferrous sulphate solution is then added in excess, and the excess back-titrated by the same permanganate. If the permanganate reduced by the nitric oxide thus formed be called A, the nitrogen present as nitric oxide is given by the formulæ:

Grms. per cubic metre	Grains per cubic foot
$N = \frac{{\cdot}007 \times A}{3V}$	$N = \frac{0{\cdot}10803 \times A}{3V}$.

In the gases freed from nitrogen and sulphur compounds by passing through these absorbents the percentage of oxygen is found by analysis in Orsat's apparatus (*v.* p. 725).

Experiments have been made by Lunge on the best forms of absorbing apparatus for the determination of nitrous fumes in exit gases; with the result of showing that a 10, or preferably 15, bulbed tube (fig. 14) is the most effective and convenient.

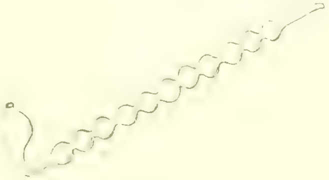

Fig. 14.

W. Crowder finds (S. C. I. 1891, 285) that the amount of oxygen present in the gases passing out of the Gay-Lussac tower is always slightly in excess of that in those passing in, as deduced from monthly averages extending over a considerable period, the increment being about

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[1] [illegible]

0·25 p.c. on the average, the gases ultimately passing out containing 5 to 5·5 p.c. Lunge explains this by supposing that air was drawn into the exit tube through some leak.

The quantity of nitrous anhydride present in the nitrous vitriol formed in the Gay-Lussac tower may be estimated by means of potassium permanganate, but is most conveniently determined by means of Lunge's *nitrometer* (fig. 15), the nitrogen compounds being converted into nitric oxide by the action of mercury, and the volume of gas produced read off; preferably the nitrometer is connected with a 'gas volumeter' (Lunge, B. 1890, 440), whereby all calculations are rendered unnecessary. The following table represents the quantities of various nitrogen compounds in milligrams corresponding with 1 c.c. of nitric oxide at 0° and 760 mm.:

NO	N	NO	N_2O_3	N_2O_5	NO_3H	NO_3K	NO_3Na
1 c.c. . .	0·627	1·343	1·701	2·417	2·820	4·521	3·805
2 „ . .	1·254	2·686	3·402	4·834	5·640	9·042	7·610
3 „ . .	1·881	4·029	5·103	7·251	8·460	13·563	11·415
4 „ . .	2·508	5·372	6·804	9·668	11·280	18·084	15·220
5 „ . .	3·135	6·715	8·505	12·085	14·100	22·605	19·025
6 „ . .	3·762	8·058	10·206	14·502	16·920	27·126	22·830
7 „ . .	4·389	9·401	11·907	16·919	19·740	31·647	26·635
8 „ . .	5·016	10·744	13·608	19·336	22·560	36·168	30·440
9 „ . .	5·643	12·087	15·309	21·753	25·380	40·689	34·245

A modified form of this apparatus is more convenient for the determination of the nitrogen in nitre (S. C. I. 1882, 15); the direct estimation of the nitrate present is obviously preferable to the usual method of determining the 'refraction,' or sum of impurities (moisture, chloride, and sulphate), and reckoning the balance as pure nitrate of sodium.

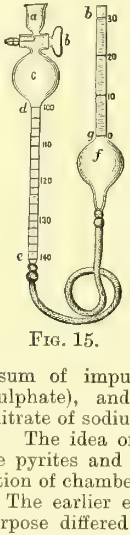

FIG. 15.

Glover tower. The idea of employing the waste heat of the pyrites and sulphur burners for the concentration of chamber acid is in itself a very old one. The earlier evaporating pans used for this purpose differed in no essential features from ordinary open coal-fired pans; but were far from generally adopted, on account of various inconveniences attending their use. Attempts to utilise the principle of a scrubber in this way were made by Gossage and others, but without any great measure of success. Thus, in 1843, a coke scrubber was employed by Muspratt, but failed on account of firing through the high temperature. Glover, however, succeeded in arranging an appliance free from this objection by using flints or other incombustible matters as packing, and so effected a threefold economy by diminishing the fuel required to raise steam, restoring to the chambers nitrous fumes absorbed in the vitriol, and rendering a cooling pipe unnecessary and thus making the temperature of the gases less variable with the weather. Further advantages also result from the use of a properly proportioned tower worked suitably (*v. infra*). Unlike many other improvements, Glover's perfected tower was not patented; so that when working descriptions of the details have not been accessible, unsatisfactory results have been occasionally obtained by manufacturers who endeavoured to utilise the principle, but did not employ the materials, arrangements, and proportions best calculated to effect the purpose.

Owing to the higher temperature of the gases, Glover towers must be far more strongly built than is necessary for Gay-Lussac towers, which in other respects they greatly resemble, the main difference being that the lead employed is much thicker, a stoutness of 20 to 25 lbs. per square foot in the upper part, and double this at the base, being often used. A thick lining of firebricks capable of resisting both heat and strong acid is employed, more especially at the lowest part, where the heat is greatest; whilst the packing consists of flints or analogous matter not disintegrated or dissolved by hot and strong acid,[1] coke being inadmissible in the hotter lower portion, although it may be used in the cooler upper part. There is always, however, some chance of the coke firing should the acid feed run short by any accident; whilst the reducing action of the coke on the higher oxides of nitrogen is not inappreciable. Moreover, the issuing acid is apt to be browned for some time after first setting up the tower, although by-and-by this ceases (fig. 16). The height is generally much less than that of the Gay-Lussac tower, from 20 to 30 feet, whilst the interior cross-section is proportionately greater, so that the cubic capacities of the two do not widely differ. Thus a Glover tower 9 to 10 feet square, and 25 to 30 high, containing 2,025 to 3,000 cubic feet, will suffice for a set of chambers containing 140,000 to 200,000 cubic feet, the capacity ratio being about 12 to 15 per mille. From 550 to 600 cubic feet per ton of sulphur burnt daily is a proportion frequently employed, the space occupied by the fire-brick lining and flint packing not being taken into account. If 20 cubic feet of chamber-space be allowed per pound of sulphur burnt daily, this represents $\frac{550}{20 \times 2240}$ to $\frac{600}{20 \times 2240} = 12·3$ to $13·4$ per mille.

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[1] In America, a particular kind of quartz rock is successfully employed, not only for the packing proper, but also for the grating supporting the packing and for the lining, the latter being prepared by carefully filling in crevices with quartz lumps of different sizes down to coarse powder so as to render the layer of packing next to the lead almost impervious to gas currents. Specially made siliceous acid-proof bricks or cylinders, glass bottles with the bottoms knocked out, and similar materials have also been successfully used.

The gases enter from the burners and pass upwards through a grating of fireclay slabs or groined arches; at the top the acid to be evaporated and denitrified is introduced by a distributing arrangement. Usually the nitrous vitriol from the Gay-Lussac tower and the chamber acid enter together; the larger the proportion of the latter, the more rapid the denitrification, but the less concentrated the acid running out hot at the base. With 48 p.c. ore the heat of the gases is usually sufficient to concentrate all the acid made (including that used in the Gay-Lussac tower) up to 145–150° Tw., and often to still greater strength; the more concentrated the acid, as a rule the less complete is the denitrification. When practicable the tower is arranged so that the vitriol to be treated flows into it from the chambers and Gay-Lussac column by gravitation, without pumping. Before being employed again in the Gay-Lussac tower the concentrated acid requires cooling. This is usually effected by passing it through a series of leaden tubes passing through a tank or trough of water (*v.* p. 758). In some works the burner gases passing through the tower are already charged with nitrous fumes from the nitre-pots; in others only non-nitrous burner gases are used, the nitre-pot vapours being led into the chambers by a different tunnel, so that the whole of the heat of the gases is not utilised. When nitric acid is used, it is sometimes fed in along with the chamber acid at the top of the tower; and when contamination of the acid with sodium sulphate is of no consequence, the nitre itself is sometimes fed in this way, dissolved in a minimum of water. Crystallisation of sodium acid sulphate and consequent blocking of the tower are said to be occasionally caused by this mode of working; apart from this defect, this mode of working is convenient when the acid is required for salt-cake making. In this case the bulk of the acid passed through the tower is only concentrated to about 140° Tw., that strength sufficing for the decomposition of salt. Only that proportion required for use in the Gay-Lussac tower is brought to a higher strength; or, if more be thus prepared, it is diluted down to 140° or so with chamber acid.

Formerly Glover towers were invariably built square, with stout wooden external scaffolding to support the tanks of acid on the top; of late years polygonal and circular towers have come into use. It is usually convenient to build the Glover and Gay-Lussac towers side by side, the former standing on a considerably higher foundation so that the tops are at the same level. The inspection and control of the two towers is thus much facilitated.

Occasionally, instead of Glover towers, other arrangements are employed to denitrate the

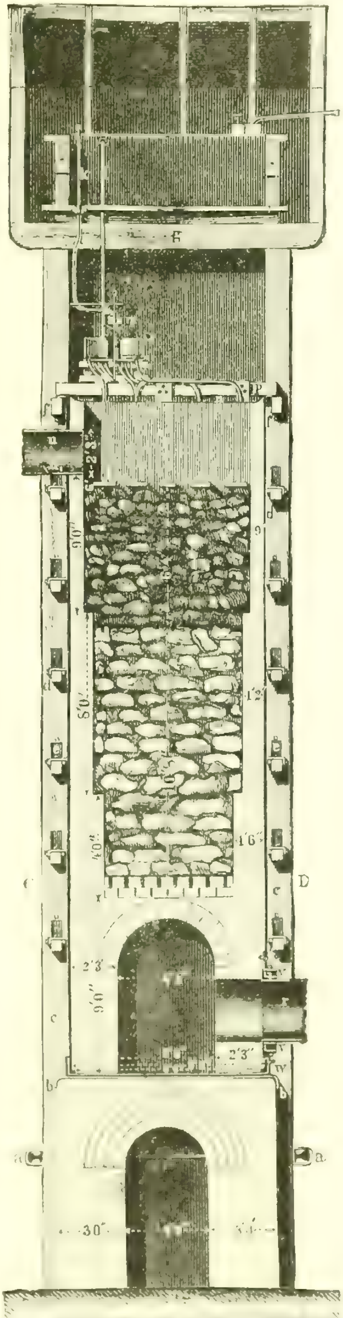

Fig. [illegible]

nitrous vitriol obtained in the Gay-Lussac columns. A denitrating tower is used at Freiburg, consisting of a stout leaden cylinder lined internally with bricks soaked in tar, and filled with silica bricks or other lumps of siliceous matter. Steam is blown in at the base, whilst the nitrous vitriol runs in through a funnel, the nitrous fumes passing off to the chamber through a flue at the top, and the dilute acid running away through the pipe at the bottom. Earthenware vessels, working in much the same fashion, are sometimes employed.

It is usually considered that in order to bring about effective absorption of nitrous fumes the acid used in the Gay-Lussac tower must be well cooled down, about 25°C. being the best working temperature. W. Crowder (S. C. I. 1891, 295) dissents from this view, finding, by direct experiment, that acid of 150°Tw. at near 100°C. absorbs nitrous fumes almost as rapidly as when at the ordinary temperature, when these fumes are much diluted with inert gases, as is usually the case in practice; if, however, the acid be hot, more rapid corrosion of the lead is apt to be brought about.

Function of the Glover tower. In addition to the advantages above stated (saving of fuel in steam raising, restoration of nitrous fumes to the chamber, and diminution of temperature fluctuations in the entering gases), the Glover tower is found to exert a marked influence on the conversion of sulphur dioxide into vitriol, this conversion taking place *in the tower itself* to a much larger extent than in any part of the chambers of the same cubical space. This partly arises from the circumstance that in the kilns a certain amount of sulphur trioxide is formed, which is filtered out, so to speak, in the Glover tower, thus causing a material diminution in the quantity of oxides of sulphur passing out of the tower, as compared with those entering it; but the sulphur burnt to sulphur trioxide present in ordinary burner gases only amounts to a few per cents. of that burnt to dioxide, whilst of the sulphur burnt in the kilns from 15 to 25 p.c. is retained in the Glover tower in the form of vitriol, so that *at least* from 10 to 15 p.c. of the sulphur burnt to dioxide becomes converted into vitriol in the tower. Scheurer-Kestner found by actual measurement that 17·5 p.c. more vitriol came out of a Glover tower than was put into it, of which about 3·5 p.c. was due to SO_3 in the gases.[1] E. Sorel (Bull. Soc. Ind. Mulhouse, 1889, 240; also S. C. I. 1890, 175) has investigated this point carefully, and finds that it is due to the accumulation and circulation of nitrous fumes in the tower. The acid entering at the top dissolves nitrous fumes, and carries them down with it until denitrated; the nitric oxide evolved during this last operation becomes oxidised and ascends, and is in part *re-absorbed by fresh acid* entering the tower *and brought down again*, and thus made to act over and over again; so that at any given instant the amount of nitrogen oxides, &c., present in the active zone of the tower is far greater than that due to the amount of nitre used, together with the nitrous fumes contained in the Gay-Lussac acid, relatively to the sulphur dioxide present. The more concentrated the acid introduced into the tower, the larger is the zone of denitrification and the better chance the nitric oxide has of being re-oxidised and absorbed so as to be carried down again; if, on the other hand, the acid be weak, a rapid diminution is brought about in the amount of nitrous fumes in circulation in the tower, and a much smaller vitriol production is brought about therein. But even when the acid is concentrated the result is not satisfactory if the top part of the packing is cold, as the acid becomes diluted by absorption of aqueous vapour. Three causes produce such cooling action: (1) the tower may be too small in sectional area, in which case the acid falls in large quantities on the first layers and cools them; (2) the tower may be too high, so that the gases get cooled too much before reaching the top; (3) the tower may be exposed to wind. As regards this last cause, a great improvement in the working of a Glover tower has been found to result when it was shielded from the wind.

Cooling of concentrated tower acid. Acid concentrated in the Glover tower or otherwise must be cooled before use in the Gay-Lussac tower; various forms of cooler are in use, generally constructed of lead, which metal has a very low conducting power.

W. Crowder gives the following temperatures as the average successive falls observed when acid at about 280°F. passed through an open cooler 41 feet long with 12 double channels for acid, so that the acid traversed nearly 500 feet. Through the interspaces between the double channels water passed in the opposite direction, as also under the bottom of the cooler (S. C. I. 1891, 295). At first the fall to 216°F. was rapid, but subsequently much slower. From 216° downwards the falls in temperature were

Fall after	passing along	1st	channel,	15°F.
,,	,,	2nd	,,	15°
,,	,,	3rd	,,	17°
,,	,,	4th	,,	13°
,,	,,	5th	,,	7°
,,	,,	6th	,,	6°
,,	,,	7th	,,	8°
,,	,,	8th	,,	3°
,,	,,	9th	,,	5°
,,	,,	10th	,,	4°

B. E. R. Newlands proposes (S. C. I. 1889, 10) to make the end of the cooling apparatus of copper, so that the further cooling of the partially cooled acid may be more quickly effected in virtue of the high conducting power of that metal; corrosion is not likely to occur, as the vitriol is denitrated; strong acid has so little effect on copper that drums of that metal may be conveniently used for its transport.

Usually the tower acid contains a notable amount of ferric sulphate &c. in solution whilst hot, mostly deposited on cooling as a crust; this circumstance renders open coolers preferable to those where the hot acid passes through pipes cooled externally, the crust being more easily removed when necessary.

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[1] Admitting that the cubic contents of the tower are about 550 cubic feet per ton of sulphur burnt daily, whilst the chamber-space is about 40,000 cubic feet, it results that if $\frac{1}{6}$ of the total vitriol is made in the tower, 550 feet of tower-space are as effective as 8,000 of chamber-space; *i.e.* the tower is more than 14 times as effective as the same amount of chamber-space. When allowance is made for the space occupied by the lining and packing, and for the fact that nitrous fumes are only liberated in the upper half of the tower, it results that the active space in the tower is *at least* 100 times as efficient as the same volume of chamber-space; from 180 to 224 times as efficient, according to Lunge ('Sulphuric Acid,' 1891, p. 601).

10. Purification and Concentration. All pyrites acid, especially when concentrated by the Glover tower, invariably contains more or less iron, arsenic, and other substances derived from the pyrites employed, in addition to lead sulphate produced by the corrosion of the chambers. Occasionally the chamber acid is treated with reagents for the purpose of removing impurities, more especially arsenic; *e.g.* it is heated with common salt, whereby arsenic is volatilised as chloride; or is treated with metallic sulphides, or thiosulphates, or with sulphuretted hydrogen, whereby arsenic is precipitated as sulphide. When nitrous compounds or nitric acid are present, it is desirable to remove them before concentrating the acid to O. V. in platinum vessels, otherwise corrosion is brought about; this is most conveniently effected by heating with ammonium sulphate, whereby nitrate or nitrite of ammonium is formed, decomposed entirely by heat, with evolution of nitrogen as such or as nitrous oxide. Non-volatile impurities are best removed by distillation of the concentrated acid; a certain proportion is often removed during concentration, being less soluble in the stronger acid, and so thrown out of solution. Lead sulphate behaves in the opposite way, being precipitated on dilution.

Before the invention of the Glover tower, chamber acid of 110° to 120°Tw. was always evaporated down, in order to concentrate it, in leaden pans, until the sp.gr. rose to about 145–150°, when the action on the lead became too rapid for further continuance. Such pans are still in use to a considerable extent; when contamination with substances derived from the fuel is immaterial they are heated by passing the flame *over* the liquid (top-firing); in other cases they are heated from below, the lead being protected from direct contact with the flame by iron supporting plates. Waste heat from various sources is often utilised for heating the pans; in some works they are mounted on the top of the kilns, or the gas flue proceeding therefrom, so as partly to utilise the heat of combustion of the sulphur burnt. For this purpose Glover successfully employs a large platinum dish placed *inside* the gas flue, a constant stream of weaker acid running in, whilst acid at 140°Tw. continuously passes out. L. Kessler leads a current of heated air through the acid contained in an apparatus of lead and stone; according to Hasenclever, this arrangement is in use at Clermont-Ferrand with satisfactory results. High pressure steam passing through leaden coils or multitubular evaporating pans is sometimes employed instead of directly fired pans. To obtain O. V., glass or platinum stills are employed, acid concentrated by the Glover tower, or in leaden pans, being introduced and subjected to heat until the great bulk of the water present is evaporated, little or no acid passing over until the last stages of the operation. In this way an acid containing about 98 p.c. of actual H_2SO_4, with some 2 p.c. of surplus water, is obtainable (although somewhat less concentrated acid, 93 to 95 p.c., is usually prepared); but heat alone will not produce any further concentration, acid of this strength boiling and condensing again unchanged. Till comparatively recently, a separate still was employed for each batch of acid worked, a number of retorts being arranged in a bench and worked simultaneously, each being filled up with the weak acid and heated until sufficient concentration by evaporation was attained, when the heat was withdrawn and the hot acid siphoned off into carboys through a platinum siphon provided with an outer jacket through which water circulated, so that the acid was sufficiently cooled by passing through; with glass retorts (set in sand baths) draughts of cold air must be scrupulously avoided, especially towards the close of the operation, otherwise great loss by breakage is apt to be occasioned, the retorts readily cracking when hottest. A much better method is the *continuous system* of Gridley, consisting in arranging a series of evaporating vessels at slightly different levels, each being connected with the next lower one by a siphon, so that when weak acid is run in to the top one, entering at its highest part, the partly-concentrated heavier acid passes through the siphon into the next, and so throughout the series, concentrated O. V. emerging from the last one of the series. In this way a slow continuous stream of acid is allowed to enter at the top, while a continuous discharge of rectified O. V. goes on at the bottom.

G. Veitch has patented (S. C. I. 1889, 983) the use of a series of flat-bottomed glass retorts, arranged one above another on a stepped terrace placed within a fire-flue, and so connected together by means of tubes that the acid fed in in a constant stream at the upper end travels through the whole series, passing out from the lowest retorts highly concentrated. The flue is tapered, the fires being placed at the lowest and widest end; the necks of the retorts are covered by asbestos millboard, to shield them from draughts, and pass into a flue.

Négrier has patented (S. C. I. 1891, 46) a similar arrangement, where porcelain dishes are used instead of glass retorts, the lip of one dish projecting over the next below in the series, so that the acid enters at the top and gradually flows through the series of dishes downwards. Two series of dishes are mounted side by side, fed from the same supply cistern, each dish resting on asbestos tissue, and surrounded by sand up to the level of the upper rim; the supporting shelves are of iron. Kretzschmar reports on the Négrier system very favourably as regards economy, but adds that the plant requires more space and attention than platinum stills.

Platinum stills are rapidly acted upon by vitriol when traces of nitrous acid are present; but when freed from that impurity by boiling with ammonium sulphate, the rate of corrosion becomes so slow as to be almost inappreciable (Scheurer-Kestner). Platinum-iridium (containing 10 p.c. of iridium and upwards) is much less readily affected than pure platinum. The loss of platinum by corrosion has been variously estimated at from 0·5 to 5·0, or even 10·0 parts, per 1,000 of O. V. made in the still, according to the purity of the acid concentrated and the state of the platinum surface, new smooth vessels being much more slowly attacked than old corroded ones.

W. C. Heræus (Chem. Zeit. Rep. 15, 36; also S. C. I. 1891, 460) found that platinum-iridium alloys containing respectively ·01, 5·0, and 10·0 p.c. of iridium, are affected by hot sulphuric acid in the relative proportions 100, 73, and 58, when sheets of these alloys are allowed to remain for 40 days in a concentration apparatus, making 98 p.c. acid. Pure platinum, commercial platinum containing 0·5 p.c. iridium, 10 p.c. platinum-iridium alloy, and pure gold, in another similar series of experiments, lost respectively 100, 90, 58, and 13 parts by weight. Accordingly, gold solder would seem to be preferable for the construction of apparatus. A process has been patented for covering the surface of platinum vessels with a compact adhesive layer of gold; this is effected by heating sheet platinum to a temperature above the melting point of gold and pouring melted gold over it, the resulting compound sheet being then rolled out to any required thickness (Patent 2,499, 1891). Notwithstanding the higher price of gold, the diminution by corrosion during use offers considerable pecuniary advantage. Several large German works have adopted this system. Lunge states (S. C. I. 1892, p. 522) that the experience gained in these works indicates that the additional cost of a Heræus still is paid for in from one to two years by the saving in platinum and repairs. Ordinary gilding is too porous to be of any practical value.

A number of other arrangements for working continuously have been proposed by different inventors, the concentration being effected by some in glass vessels; by others in platinum ones of varying shape, preferably with corrugated bottoms; by others in cast-iron retorts. In the last case, whilst the final concentration is thus practicable, inasmuch as acid approaching towards the strength of SO_4H_2 has little or no action on iron, weaker acid cannot be successfully evaporated in this way on account of the corrosion brought about; the final acid, however, is not seriously contaminated with iron, inasmuch as the sulphate mostly separates as an insoluble precipitate as the acid becomes fully concentrated.[1]

The formation of this precipitate similarly occurs when chamber acid is concentrated in leaden glass or platinum pans and stills, more especially when Glover tower acid is used, owing to the greater proportion of flue-dust then present in the gases; the crusts thus formed in platinum vessels require periodical removal (by solution in hot water), otherwise the platinum is rapidly destroyed.

When acid of higher strength than ordinary O.V. of 94 to 95 p.c. H_2SO_4 is required (*e.g.* in the formation of nitro- compounds such as gun cotton and in the manufacture of certain organic sulphonic acids), one method adopted is to add fuming acid in such quantity that the free sulphuric anhydride in the latter may just suffice to convert all the surplus water in the O.V. into monohydrated acid H_2SO_4; another, due to Lunge and Marignac, is to freeze out monohydrated acid from commercial O.V. by suitably chilling it, separating the crystals from the fluid portion, and thawing the former. The former is a much more costly operation than the latter; thus taking Lancashire market prices for 1889—viz. 2*l.* 15*s.* 6*d.* for 95 p.c. O.V. and 13*l.* for fuming acid containing 50 p.c. SO_3—Lunge calculates ('Sulphuric Acid,' 1891, 2nd ed. p. 738), that as 4·44 parts of the latter are requisite per 100 of the former, or 8·88 cwts. per ton, the cost of the H_2SO_4 thus prepared is 5*l.* 17*s.* 8*d.*, or more than double that of the original O. V.; whereas the freezing-out process adds on far less to the cost.[1] This manufacture is thus carried out by the Malétra Company, who have obtained the monopoly for France. The acid is first concentrated in the ordinary way, preferably up to about 97 p.c., as then the mother-liquors contain about 95 p.c., and can be sold without requiring further concentration. A pipe provided with a tap connects a filling machine with a reservoir of concentrated acid at a higher level; this machine has a capacity just equal to that of each set of crystallising cells, and is divided into as many compartments as there are cells in the set, each compartment being connected with a corresponding cell by a pipe, the end of which almost touches the sloping bottom of the compartment, passing upwards through an air-tight cover to a height slightly above that of the acid in the reservoir, and then bending downwards, ending above the crystallising cell. When the cells are not being filled, the exposed end of the pipe is closed by a dripping vessel. The machine is filled by gravitation from the reservoir, and then by means of compressed air the acid is forced over into the cells, each of which holds about 12½ kilos. of acid; these are placed in a solution of calcium chloride cooled by a refrigerating machine to −20° C. The acid, frozen into blocks, is loosened from the sides of the cells by dipping them for an instant into hot water, the blocks being then broken up by an Archimedean screw, drained by a hydro-extractor, melted, and packed for transport. Acid of 100 p.c. H_2SO_4 is thus readily obtained (Osterberger and Capelle, Bull. Ind. Soc. Rouen, 1889, 307; Chem. Ind. 13, 48; also S. C. I. 1890, 390 and 507).

A similar arrangement has been patented in Britain (S. C. I. 1888, 209); the freezing cells are filled from a 'charging box,' divided into compartments, the acid being expelled by compressed air simultaneously from each compartment into the cell in connection with it; by means of a crane the cells are moved into the freezing tank, which contains a number of rows of cells. The row that has been in longest is lifted out, each other row moved a step forward, and the row of cells to be introduced placed in the last vacant position.

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[1] Iron drums for the transport of O. V., as well as of fuming acid, can similarly be employed instead of glass carboys.

[1] Exact details as to the actual cost of freezing out do not appear to have been published. Majert and Messel have patented (March 26, 1873) a peculiar method for effecting the concentration of chamber acid, consisting of a kind of washing of the pyrites burner gases with limited quantities of acid, whereby the sulphur trioxide present is converted into sulphuric acid by the excess of water in the acid. Of course the resulting product is apt to be rendered highly impure from the arsenious oxide, dust, &c., carried over along with the gases from the burners, besides being saturated with sulphur dioxide; concentrated acid thus prepared does not seem to have found its way into the market to any great extent.

Solidified sulphuric acid (*consolidated acid*). The transport of oil of vitriol, whether by land or sea, is attended with considerable risk of damage by leakage from the containing vessels; accordingly, very high rates of freight are usually charged, rendering the substance much more costly at a distance from the factory than would be the case with a less destructive material. To obviate as much as possible the danger of leakage, various proposals have been made, and to some extent carried into practice, for 'consolidating' the acid into a nearly solid mass by the addition of some suitable solid material that will not interfere with the subsequent uses of the acid. For this purpose Vorster and Grüneberg use *kieselguhr*, such as is employed in the dynamite industry for 'solidifying' nitroglycerine. Oil of vitriol mixed with 25-30 p.c. of kieselguhr becomes completely solidified, so that it can readily be transported by land or sea in lead-lined iron vessels without risk of damage through leakage (S. C. I. 1884, 134, Germ. Pat. 24,748, June 3, 1883). On adding water and allowing to settle, the kieselguhr subsides, and may be collected for use over again; whilst a diluted acid is obtained available for aerated-water manufacture, evolution of chlorine from bleaching-powder for treating auriferous quartz, and such-like purposes. White and Rickmann (Eng. Pat. No. 17,095, 1887) similarly employ various saline substances, such as alkaline sulphates and sulphate of calcium; on ultimately treating the consolidated acid with water, these solidifying agents either subside like kieselguhr, or dissolve with the acid, their presence in the solution not interfering with the use of the fluid for aerated-water manufacture, &c. By heating mixtures of sulphuric acid and proportionate quantities of sodium or potassium sulphate so as to drive off excess of water, substances are obtained capable of setting hard on cooling, and crystallising so as to form masses readily transported from place to place without difficulty or risk. According to Giles, Roberts, and Boake (Patent Specification 11,979, 1890), a 'pentasulphate' of sodium can be thus formed, having the composition $Na_2O,5SO_3,3H_2O$, or anhydrosulphate of sodium combined with sulphuric acid, $Na_2O,2SO_3,3H_2SO_4$. Brindley (Patent Specification 17,796, 1891) obtains analogous compounds by either using somewhat less acid or not heating so strongly, the following boiling temperatures corresponding with the annexed compositions:

$$200^\circ\text{C.}\begin{cases} NaHSO_4.H_2SO_4.H_2O \\ KHSO_4.H_2SO_4.H_2O \end{cases}$$

$$260^\circ\text{C.}\begin{cases} 2NaHSO_4.2H_2SO_4.H_2O \\ 2KHSO_4.2H_2SO_4.H_2O \end{cases}$$

$$290^\circ\text{C.}\begin{cases} 2NaHSO_4.3H_2SO_4 \\ 2KHSO_4.3H_2SO_4 \\ NaHSO_4.H_2SO_4 \\ KHSO_4.H_2SO_4 \end{cases}$$

A substance of the composition of the so-called 'pentasulphate of sodium' would furnish on treatment with water free sulphuric acid, H_2SO_4, equivalent to nearly 76 p.c. of the mass employed—*i.e.* 5 parts by weight of this substance would be equivalent to 4 parts of ordinary oil of vitriol for aerated-water making and such-like purposes. The preparation of this form of solidified sulphuric acid has been recently decided to be covered by White and Rickmann's patent.

11. Practical yield of vitriol, and losses during manufacture. From 100 parts of sulphur charged into kilns as brimstone or pyrites, less than the quantity of vitriol chemically equivalent thereto is actually obtained, unavoidable losses being experienced due to the following causes:

1. Sulphur is retained in the ashes or cinder as sulphide, sulphate &c., and sublimes unburnt.

2. Loss occurs by leakages of gas during recharging and working the kilns, re-potting, existence of leaks and crevices in the walls of chambers and tunnels &c.; leakage of liquid vitriol from chambers, siphons, tanks, &c.; and accidents of various kinds difficult in practice wholly to avoid for long periods together.

3. Sulphur escapes in the exit gases, either through imperfect conversion of sulphur dioxide into vitriol, or by incomplete filtering out from the gases of suspended vesicles of vitriol, &c.

Of the three sources of loss the first has been already partly discussed (pp. 720 *et seq.*). With Spanish pyrites, from 5 to 6 parts of sulphur out of 100 charged into the kilns are usually left in the cinder, taking the average burning throughout the year, although a somewhat smaller proportion may be often left when no derangements of working occur and everything is going to the best advantage; with inferior ores much larger amounts relatively to the sulphur charged into the kilns are uniformly left in the cinder, up to 15 parts in 100, or even more in extreme cases. When sulphur sublimes, some portion condenses in the flues as sublimate, and is ordinarily lost; part finds its way into the chambers, and if the vitriol made is subsequently submitted to heat, causes a conversion of sulphuric acid into sulphurous acid by the reaction $S + 2SO_4H_2 = 3SO_2 + 2H_2O$.

The sulphur dioxide thus formed is not lost if the change takes place in a Glover tower; but if in an ordinary evaporating pan, one equivalent of sublimed sulphur causes the loss of two equivalents of previously formed sulphuric acid in addition.

The second source of loss almost entirely depends on the nature of the plant used, and the skill employed in working it; the loss by leakage through faulty joint, crevices, corrosion, pinholes, &c., is but slight when the chambers are new, and does not amount to any considerable fraction of the make for some years if they are continually examined and kept in a state of thorough repair. But after some years use, no amount of patching can keep pace with the formation of holes through corrosion; not only are gases and even liquid vitriol thus lost from within, but much air is drawn into the chambers, diluting and cooling the gases and impeding their reaction, and diminishing the yield by increasing the loss from cause No. 3 unless a proportional reduction in sulphur burnt is made.[1]

A. Burgemeister (Chem. Zeit. 13, 1633; also S. C. I. 1890, 66) has made various measurements of the rate of diminution in thickness of the lead; in the case of a No. 1 chamber, during 120 months, the thickness of the walls was originally 3·4 millimetres, and at the end of the period averaged 2·8, the diminution being at the rate of 6·84 kilos. per square metre: here the temperature was 65° to 90°C. In the case of a No. 2 chamber the original thickness was 2·57 millimetres, and after 210 months' working (not including 75 months lying idle), the average thickness was 1·88 millimetres, or 7·86 kilos. per square metre.

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[1] [illegible]

Average monthly loss, No. 1 chamber, ·0570 kilos. per square metre.

Average monthly loss, No. 2 chamber, ·0374 kilos. per square metre.

Those parts of the walls in contact with the acid lying in the chambers are most acted upon, holes being eaten through in places. Next come the parts where the lead overlaps, and the wooden framework prevents its cooling. When the seams are burnt from the inside, an overlapping strip is left outside, and in such places the inner thickness of lead is soon eaten through and the seams leak. If, on the other hand, the seams are burnt from the outside, they do not leak until the outer sheet is also eaten through. The floor is the part of the chamber least acted on, the acid covering it not corroding the lead as rapidly as the gases, on account of the lower temperature (40°–50°C.).

Practice differs much amongst manufacturers as to how long it is possible to work a chamber economically; some consider that 10 to 12 years' good work can be got out of a chamber, or even more when brimstone is burnt. Lunge states that on the Continent, where vitriol chambers are not so much strained as is usually the case in England, 20 or even 30 years' duration is possible. Others regard it as more profitable in the long run to rebuild after 7 or 8 years' working at the most, or even 5 years, especially the first chamber of a series; considering that the cost of repairs that would be necessary did the chambers stand longer, the injury to other plant through leakages, and the larger loss through diminished make and yield, would more than counterbalance the cost of earlier re-erection. Obviously, no general rules can be laid down in such cases; what might be defensible and even wise under certain conditions, might be a most detrimental policy under others.[1]

As regards the third source of loss, the amount of incomplete conversion mainly depends in the first place upon whether Gay-Lussac and Glover towers are used or not. If they are used, then the amount of escaping sulphur dioxide cannot possibly amount to more than about 2 p.c. of that equivalent to the sulphur burnt, otherwise an enormous loss of nitre is also occasioned through formation of abnormally large amounts of nitric oxide not absorbed in the Gay-Lussac tower; with proper working in this respect the loss by incomplete conversion of sulphur dioxide into vitriol may be brought down well below 1 p.c. for considerable periods of time together, and, even taking into account unavoidable accidents and derangements of plant and extra losses on re-starting after repairs &c., may be reduced to distinctly less than 2 p.c. one year with another. But, to effect this, firstly an amount of chamber-space of 18 to 20 cubic feet at least per 1 lb. of sulphur burnt (as Spanish pyrites) per day is requisite; nextly, the state of repair of the chambers must be efficient, and the Gay-Lussac column well proportioned and packed and carefully worked; thirdly, a considerable amount of highly-skilled supervision must be exercised; and fourthly, an adequate proportion of nitre must be employed, increased or diminished as occasion requires from time to time so as always to preserve the proper working proportion of nitrous fumes in the chambers, this proportion of nitre averaging one year with another usually *over* 3 parts per 100 of sulphur burnt, although at times it may be reduced to 2·5 or even below 2. Under such conditions 100 parts of sulphur charged into kilns may be accounted for thus:

Left unburnt in cinder .	5 to	6 parts
Accidents, leakages, and defective conversion, stoppages for repairs, &c.	2 to	3 ,,
Yield in the form of chamber acid	93 to	91 ,,
	100	100

the yield of chamber acid for shorter periods under the most favourable circumstances reaching as high as 94 or even 95 p.c.; with, of course, proportionate amounts of falling off to 90 or even 85 p.c., when inferior pyrites is used, and according as the condition of the plant and working generally are further removed from the highest state of efficiency. The season of the year somewhat influences the yield by affecting the mean temperature of the chambers. According to Lunge, in the warmer climates, even with efficient chamber-space, the yield during the summer months is always some 3 p.c. less than that in winter.[1]

When Gay-Lussac and Glover towers are not used, the proportion of sulphur acids escaping in the exit gases is always greater than when they are used; with an amount of chamber-space not less than 25 cubic feet per lb. of sulphur burnt daily (as Spanish pyrites), and with a nitre consumption of 10 p.c. of the sulphur burnt, the state of repair and general supervision being good, this source of loss may be reduced to about 5 p.c. for considerable periods together, or say 6 to 7 p.c. including accidents, leakages, and irregularities; leading to the statement for one year with another:

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[1] When profits are cut down to a minimum, as in the Leblanc process with its allied industries, and especially when the output is limited by considerations of trade policy, obviously it will answer best to diminish all sorts of working losses as much as possible, rather than to attempt to make a larger quantity with somewhat increased amounts of loss through deficient yield &c.; but, under other conditions, it may often pay better to sacrifice a small portion of the yield, and obtain a larger total output. Thus, to take an extreme illustration, it would be less profitable to sell 100 tons weekly of a given article when the total cost of production was only 95 p.c. of the selling price, than it would to sell 150 tons weekly when by reason of diminished yield &c. the cost of production was raised to 96 p.c. of the selling price, assumed to be the same as before; the total profits in the two cases being as 5 × 100 to 4 × 150, *i.e.* as 5 to 6.

[1] Exact details concerning the yield of sulphuric acid obtained when the French system of 'forced working' ('production intense,' p. 737) is adopted do not appear to have been published. According to Sorel, with a chamber-space of only 11·5 cubic feet per pound of sulphur burnt, and a nitre consumption of 2·26 per 100 of sulphur burnt, 50 p.c. pyrites being employed, and so well burnt that the cinders only contained 0·8 p.c. of sulphur (!), a yield was obtained at l'Oseraie of 148·81 parts of H_2SO_4 per 100 of pyrites consumed, equivalent to slightly more than 300 of H_2SO_4 per 100 of sulphur burnt; and representing a yield in the form of sulphuric acid of upwards of 97 p.c. of the sulphur contained in the pyrites—an incredibly high result.

Left unburnt in cinder .	5 to 6	parts
Defective conversion, leakages, &c. . .	6 to 7	„
Yield as chamber acid .	89 to 87	„
	100 100	

the yield rising to 90 p.c., and even more, for short periods of time under the most favourable conditions; but, inasmuch as all the necessary conditions for maximum yield are comparatively rarely found in works unprovided with Gay-Lussac towers, 80 to 85 p.c. is more nearly the quantity actually obtained under such circumstances; with even smaller proportions in extreme cases, especially when low-class sulphur ores, coal-brasses, &c., are used.

With brimstone chambers employing Gay-Lussac towers to the best advantage, 97 to 98 p.c. of the sulphur burnt may be obtained in the form of chamber acid, with a nitre consumption of 3 to 4 parts per 100 of sulphur burnt; and when no Gay-Lussac towers are used, with a nitre consumption of 6 or 7 p.c. of sulphur, and a chamber-space of 25 to 30 cubic feet per lb of sulphur per day, 95 p.c. and upwards of the sulphur burnt may, with good management and first-class plant, be obtained as chamber acid; and proportionately smaller percentages under less favourable conditions.

In all cases a somewhat smaller yield is generally obtained when O. V., is made on account of losses by volatilisation, decomposition, breakages, &c., during concentration.

As regards the loss of nitre, both with and without Gay-Lussac towers, the figures obtained in different factories necessarily vary very considerably; but in general the causes of loss do not lie very far from the following values:—

—	With G.-L. towers	Without G.-L. towers
Nitre used per 100 parts of sulphur burnt . .	2·5 to 4	About 10
Percentage of nitre lost in exit gases and retained in the chamber acid: leakages	15 to 30	Not exceeding 50
Ditto lost by secondary reactions in the chambers &c. (reduction to N_2O and nitrogen)	85 to 70	At least 50
	100 100	100

With 'forced work' it is stated that the nitre consumption does not materially exceed the ordinary amount as above tabulated. Notwithstanding the much larger proportion of nitrous fumes kept in circulation, the loss by defective absorption &c. in the Gay-Lussac tower is reduced to the usual limits by employing very much larger nitre recovery plant; whilst no considerable increment appears to be occasioned by the loss of available oxides of nitrogen through secondary reactions. Thus Sorel states that when only 14 cubic feet per pound of sulphur burnt per day was allowed at l'Oseraie the nitre consumption was only 1·03 per 100 of H_2SO_4 made, representing about 3·3 parts per 100 of sulphur burnt; a result comparable with good average working over long periods in works where 18 to 20 cubic feet are allowed with nitre recovery plant of ordinary dimensions. During another period only 11·5 cubic feet per pound of sulphur was allowed, whilst the nitre consumption was booked as only $2\frac{1}{4}$ per 100 of sulphur burnt.

Cost of production. Lunge gives the estimates on next page, the first four being the results of his own experience when pyrites was burnt, the vitriol produced being of gravity 140-144° Tw. the others derived from Karl Stohmann, Lacroix, and Favre ('Sulphuric Acid,' 1891, 2nd ed. pp. 765 *et seq.*).

The following comparative estimate of the cost of manufacture of brimstone and pyrites acid in America has been given by W. G. Cranshaw (S. C. I. 1883, 413), the chamber used having a capacity of 110,000 cubic feet:—

Brimstone.

Cost of plant, $30.000

1,100 tons at $31·50 . .	$34.659
88 tons saltpetre at $55 .	4,840
Wages	1,200
Coal	1.200
Interest, repairs, &c., at 20 p.c.	6,000
	$47,890

Produce, 4.950 tons chamber acid, costing per ton $9·71.

Pyrites.

Cost of plant, $32,000

2,100 tons at $6 . . .	$12,600
80 tons saltpetre at $55 .	4.400
Wages	1,200
Coal	1,200
Interest, repairs, &c., at 20 p.c.	6,400
	$26.200

Produce 4,050 tons chamber acid, costing per ton $6·47.

Lunge regards these figures as misleading, and intended to represent the pyrites manufacture as much cheaper relatively than is really the case, much more plant being required for pyrites kilns, breakers, &c., than represented by the extra $2.000 charged to this account, and much more nitre relatively to brimstone being required. Moreover, the cost of repairs and wages are necessarily much higher with pyrites plant than with brimstone plant. Both brimstone acid and pyrites acid are represented as having the same market value, instead of the latter being of less value on account of impurities, especially arsenic and iron.

—	Belgium smalls, containing 40 p.c. sulphur, at 18*s.* 8*d.* Coals at 4*s.* 6*d.*				Norwegian and Westphalian pyrites, containing 42 p.c. sulphur, at 23*s.* 6½*d.* No Gay-Lussac tower				Cuprous Norwegian ore. Gay-Lussac and Glover towers used. 1873. Pyrites at 25*s.* 6*d.* Coals at 10*s.*				Cuprous Spanish ore, at 19*s.* 1876. Coals at 4*s.*			
	Ton	£	*s.*	*d.*	Ton	£	*s.*	*d.*	Ton	£	*s.*	*d.*	Ton	£	*s.*	*d.*
Pyrites	1·048	0	17	5·6	·9795	1	3	0	·838	1	1	4·4	·758	0	14	4·8
Nitre	·044	0	6	7·2	·0393	0	12	7	·0172	0	4	1·5	·0145	0	3	2·3
Coals	·557	0	2	6·1	·125	0	0	6	·171	0	1	8·5	·250	0	1	0·0
Ordinary wages		0	6	2·2		0	7	5		0	6	9·5		0	3	6·0
Repairs, &c.		0	5	0·6		0	2	0		0	1	10·5		0	1	6·0
		1	17	9·7		2	5	6		1	15	10·4		1	3	7·1
Deduct value of nitre cake		0	1	1·2		0	1	6								
Cost per ton of O.V.		1	16	8·5		2	4	0								

	Belgium pyrites at 35 p.c.		Switzerland pyrites		France pyrites at 40 p.c.		Marseilles brimstone	
	Kilos	Francs	Tons	Francs	Kilos	Francs	Kilos	Francs
Pyrites / Brimstone	1,000	35·0	2½	112·50	640	19·20	1,000	170·00
Nitre	42	15·96	0·17	75·82	18	6·84	75	30·00
Wages		3·00		14·00		3·26		4·00
Coals	150	1·80		59·80	80	2·40	100	2·50
Repairs and general expenses		3·00				6·20		6·50
		58·76		262·12		37·90		213·00
Deduct nitre cake	. . .	. . .	. . .	. . .		1·00		
						36·90		
Produce	1365 kilos acid at 53°B.; or 43·0 francs per 1,000 kilos		5 tons 5 cwts. acid at 50°B.; or 50 francs per ton		1,000 kilos acid at 50°B.; or 36·90 francs per 1,000 kilos		4,000 kilos acid, at 53°B.; or 53·2 francs per 1,000 kilos	

The following figures are quoted from the Mineral Resources of the United States,' 1886:—

Brimstone.

1 ton (= 2,000 lbs.) brimstone at 98 p.c.	$19·00
50 lbs. nitre at 2·5 cents per lb.	1·25
5 cwts. coal at $4 per ton	1·00
Wages	2·25
Superintendence and management	2·00
General jobbing repairs	0·50
Interest on capital ($75,000 at 10 p.c.)	4·60
	30·60

Produce 4½ tons acid at 50°B.
Cost per ton $6·80

Pyrites.

2½ tons pyrites at 46 per cwt.	$11·50
60 lbs. nitre	1·50
5 cwts. coal	1·00
Wages	2·00
Superintendence and management	2·00
General jobbing repairs	0·60
Interest on capital ($100,000 at 10 p.c.)	6·15
	25·75

Produce 4½ tons acid at 50°B.
Cost per ton $5.50

More recent estimates of the relative cost in the United States of pyrites acid and brimstone acid have been given by W. H. Adams and J. H. Kelley (S. C. I. 1892, p. 814, from Eng. and Mining J., July 23, 1892). According to Adams, sulphur in the form of pyrites is much cheaper than brimstone in the States, because the latter must be imported whilst the former is largely indigenous. He gives the following comparison of the cost of producing 18 tons of chamber acid daily by the two processes:—

Cost of pyrites acid.

10 tons pyrites, including freight, losses in transit and burning &c., producing 18 tons daily; at $5 per ton	$50·00
Nitrate of soda, about 4½ p.c. on sulphur contents; say 400 lbs. at $2·50 per 100 lbs.	10·00
Coal 2 tons daily at $3 per ton	6·00
Labour: five men for all purposes at $1·25 per day	6·25
Superintendent and office cost	6·00
Wear and tear per day: 10 p.c. per annum on works costing $35,000	10·00
Total	$88·25

$4·90 per ton of chamber acid.

Cost of brimstone acid.

4 tons brimstone, all costs as above at $24 a ton	$96·00
Nitrate of soda: 6 p.c. of brimstone used or 538 lbs. per day at $2·50 per 100 lbs.	13·45
Labour: five men all purposes at $1·25 per day	6·25
Coal, 2 tons daily at $3 per ton	6·00
Superintendent and office cost	6·00
Wear and tear as above	10·00
Total	$137·70

$7·65 per ton of chamber acid.

Lunge's criticisms on the previous comparison by Cranshaw are obviously also here applicable. According to Kelley, the cost of producing vitriol is much the same, whether pyrites or brimstone be used. The wear and tear is calculated by him at 10 p.c. per annum for pyrites plant, and only 6 p.c. for brimstone plant, on account of the longer life of the chambers, the extra plant in the former case being valued at \$3,000 (pyrites plant, \$27,000 for a make of 9 tons acid at 50°B. daily; brimstone plant, \$30,000 dollars, using the same chambers, and making $12\frac{1}{4}$ tons daily).

Pyrites.

5 tons pyrites, at \$5 to \$8 .	\$25·00 to	\$40·00
270 lbs. nitrate, at \$2.50 per 100 lbs.	6·75	6·75
360 lbs. acid, at 40 cents per 100 lbs.	1·45	1·45
Breaking ore and loss, at 25 cents per ton . . .	1·25	1·25
Labour (4 men, at \$1·25 per day)	5·00	5·00
Wear and tear . . .	9·00	9·00
Office and other expenses .	5·00	5·00
	\$53·45 ,,	\$68·45

Producing acid at 50°B. = sp.gr. 1·53, at from \$5·94 to \$7·60 per ton.

Brimstone.

$2\frac{1}{4}$ tons brimstone, at \$21 to \$29	\$52·50 to	\$72·50
200 lbs. nitrate, at \$2·50 per 100 lbs.	5·00	5·00
200 lbs. acid, at 40 cents per 100 lbs.	0·80	0·80
Labour (2 men, at \$1·25) .	2·50	2·50
Wear and tear . . .	6·00	6·00
Office and other expenses .	5·00	5·00
	\$71·80 ,,	\$91·80

Producing acid at 50°B. = sp.gr. 1·53, at from \$5·98 to \$7·65 per ton. C. R. A. W.

Persulphuric Acid and the **Persulphates.** Persulphuric anhydride S_2O_7 was first obtained by Berthelot (C. R. 86, 20, 1878) by exposing a mixture of dry sulphur dioxide and oxygen to the influence of the silent electrical discharge in the apparatus described in A. Ch. [5] 12, 463. Later he showed that under similar conditions oxygen and sulphur trioxide united to form the same body (C. R. 86, 277). At the end of from eight to ten hours the sides of the vessel are covered with drops of a thick, viscid liquid, which at about 0° crystallises in transparent, long, flexible needles. Traces of water, nitric acid (from nitrogen), or of saline compounds (from the glass) tend to prevent crystallisation. The substance closely resembles sulphur trioxide in appearance; the crystals, however, are longer, more transparent, and more laminated than those of sulphur trioxide. It is said to possess a pungent smell (Marshall). At ordinary temperatures it is very unstable, but if the temperature be near zero it can be kept for several days. An aqueous solution rapidly decomposes, O being liberated and H_2SO_4 formed. A solution in concentrated H_2SO_4 is, however, much more stable; yet even this slowly evolves oxygen. Rise in temperature, presence of moisture, or contact with precipitate accelerates the decomposition of S_2O_7 into SO_3 and O. This tendency to give up O distinguishes persulphuric anhydride from sulphuric anhydride. It, indeed, gives the clue to most of the reactions of S_2O_7; thus S_2O_7 oxidises metallic mercury and solutions of SO_2, $FeSO_4$, $SnCl_2$, and KI even in the cold. Berthelot utilised this property in his analytical determination of the composition. By acting on the S_2O_7 with standard solutions of KI, $FeSO_4$, or $SnCl_2$ and titrating back with permanganate, he determined the amount of 'available oxygen.' The SO_3 was then determined as $BaSO_4$. The results of different analyses gave the ratio 1 to 10, which accords with the formula S_2O_7 for

$$\begin{array}{ll} S_2O_7 = & 2SO_3 + O, \\ 176 & 160 + 16. \end{array}$$

Berthelot did not succeed in isolating the acid. He, however, obtained solutions of it in H_2SO_4: (1) By the action of H_2O_2 on H_2SO_4, and (2) by the electrolysis of concentrated H_2SO_4. He, moreover, expressed his belief that solutions of persulphuric acid might also be obtained by the action of other peroxides on H_2SO_4 at a very low temperature. The reactions of electrolysed concentrated H_2SO_4 were exactly the same as those of the solution of S_2O_7 on concentrated H_2SO_4.

Berthelot has also examined the action of the electric current on *dilute* H_2SO_4 solutions, such as are used in the electrolysis of water. He found that there was an appreciable amount of persulphuric acid in solution at the anode, and concluded that the oxidising substance present in such a liquid was, as a rule, persulphuric acid, and not H_2O_2, or ozone, as had been previously believed. His conclusions may be stated as follows: The substance formed in the liquid about the positive electrode in the electrolysis of dilute solutions of H_2SO_4, which, together with the ozone, accounts for the variation of the ratio of H to O from the theoretical 2 : 1, is not H_2O_2, as generally supposed. For, as a rule, it does not—(1) reduce permanganate; (2) form perchromic acid with chromates; or (3) form CaO_2 with lime water—three very delicate tests for H_2O_2. It is also less stable than H_2O_2. Neither is the oxidising substance ozone, for it does not oxidise arsenious acid; and when shaken up with fifty times its volume of air it does not give to it any gas or volatile body capable of acting upon KI. It *is* persulphuric acid, for the oxidising substance is produced only during the electrolysis of H_2SO_4 solutions and not when solution of H_3PO_4, KOH, or $Ba(OH)_2$ is used.[1] It, moreover, answers to the properties, both positive and negative, of persulphuric acid solutions (C. R. 86, 71). Richarz (A. Ch. [2] 24, 183) in the main confirmed Berthelot's results.

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[1] It should be noted that the different observers do not agree with respect to several of the reactions of persulphuric acid. Thus, Berthelot states that it does not oxidise As_2O_3 (C. R. 86, p. 71), while Traube affirms that As_2O_3 is completely oxidised within a short time. Again, Richarz has stated that persulphuric acid in 70 p.c. H_2SO_4 solution oxidises oxalic acid, and also oxidises N to nitrous acid. Traube, on the contrary (B. 22, 1518), finds that this is not the case, and that persulphuric acid is a much weaker oxidising agent than Richarz states. This difference as to fact has considerable bearing on the views held by Richarz and Traube concerning the true nature of H_2O_2. The former, believing that its presence at the anode is due to the chemical action of persulphuric acid on water, regards it as HO.OH, whilst Traube, not admitting the possibility of the oxidation of water by persulphuric acid, considers it as an 'oxygen-molecule compound,' and represents it as H.O : O.H.

He found, however, that small quantities of H_2O_2 and ozone are formed together with the persulphuric acid, the relative amounts varying with the strength of the acid electrolysed. Thus with strengths up to 40 p.c. little or no hydroxyl was formed. With strengths from 40 to 90 p.c. the amount of H_2O_2 gradually increases (max. probably with 70 p.c. solutions). To estimate H_2O_2 in presence of persulphuric acid, Richarz recommends a solution of titanic acid in H_2SO_4. This gives an intensely yellow precipitate, which decolourises the same amount of permanganate as the H_2O_2 which goes to form it. Permanganate can also be used directly, as persulphuric acid does not reduce it. See also Richarz, A. Ch. [2] 31, 912, and McLeod, C. J. 1886, p. 591.

Persulphuric acid sometimes exerts a reducing action. For example, PbO_2 is converted into $PbSO_4$ when brought into a 40 p.c. H_2SO_4 solution of persulphuric acid. Similarly, MnO_2 and AgO are converted into the sulphates with evolution of O. The similarity here to the behaviour of H_2O_2 was quoted by Traube in support of his formula $(SO_2)O_2$. But, since O is evolved in the reactions, they may be equally well explained on the assumption that the formula is S_2O_7. Indeed, the only result given by Traube which cannot be so explained is that showing the ratio of available O to SO_3 formed on decomposition. To obtain this ratio Traube diluted a 40 p.c. H_2SO_4 solution with 2–4 times its volume of water and added freshly-prepared barium phosphate to remove the H_2SO_4. The amount of active O in the filtrate was then determined by adding $FeSO_4$ and titrating back with permanganate. The SO_3 was estimated by boiling a solution with $BaCl_2$ and weighing the $BaSO_4$ produced. The ratio of the weights was found to be 1 : 5, which agreed with the empirical formula SO_4. But Traube overlooked the possibility of the presence of H_2O_2 (Berthelot), and also the possibility that some of the substance might remain undecomposed on boiling (Marshall).

Hugh Marshall discovered that crystals of potassium persulphate were formed at the anode during the electrolysis of a solution of the sulphates of Co and K in a 'divided cell.' He found that the same substance could be prepared by the electrolysis of a saturated solution of $KHSO_4$ in the same apparatus. The Am salt was prepared by substituting Am_2SO_4 for $KHSO_4$. By treating a saturated solution of the Am salt with $Ba(OH)_2$ he obtained the Ba salt, the excess of $Ba(OH)_2$ being removed by CO_2. The Pb salt was obtained by decomposing a solution of the Ba salt with H_2SO_4 and neutralising the liquid with $PbCO_3$. By acting upon the Ba salt with $ZnSO_4$, a solution of the Zn salt was obtained. Attempts to isolate the persulphates of Cu, Na, Li, and Mg were unsuccessful.

The formulæ at which he arrived were KSO_4, $AmSO_4$, $Ba(SO_4)_2$, $4H_2O$ and $Pb(SO_4)_2,3H_2O$ (?). The choice of KSO_4 instead of $K_2S_2O_8$ which Berthelot gave, was based upon the determinations of the conductivity of dilute solutions. These gave: $\Delta = (\mu_{1024} - \mu_{64}) = 15{\cdot}7$. Now, in the case of potassium perchlorate $\Delta = 15$; hence it is probable that the formulæ are of the same type. It must be noted, however, that the persulphates and perchlorates do not appear to be isomorphous, for the former appear to belong to the asymmetric system. It is rather remarkable that the K salt appears to be the least soluble. Thus, 100 parts of water at 0° dissolve

1·77	parts of	KSO_4
58·2	,,	$AmSO_4$
52·2	,,	$Ba(SO_4)_2,4H_2O$.

Exact determinations in the other cases have not been made, but the salts are all very soluble.

Solutions of persulphates give no precipitate with $BaCl_2$; on warming, however, $BaSO_4$ slowly separates and Cl is evolved. The aqueous solutions gradually decompose, a sulphate being formed and O being liberated. Iodine is liberated from KI solution. On ignition of the salts containing fixed bases a sulphate is left, SO_3 and O being evolved. A solution of $Pb(OH)_2$ in KOH yields a precipitate of PbO_2 on boiling. The action with $AgNO_3$ seems to be: $H_2O + AgNO_3 + M'SO_4 = AgO + MHSO_4 + HNO_3$. Fehling's solution gives a red precipitate of Cu_2O; $FeSO_4$ is rapidly oxidised to ferric sulphate with rise of temperature. Organic colouring matters are bleached; alcohol is oxidised to aldehyde in presence of water. With neutral cobaltous and manganous salts a partial precipitate of Co_2O_3 and MnO_2 is obtained on heating. In the cold the addition of alkalis to a solution of KSO_4 and manganous, cobaltous, or nickelous salts precipitates the lower oxides, which immediately darken, forming higher oxides. Paper and cloth become quite rotten after being dipped in a solution of persulphate. K_4FeCy_6 is readily oxidised to K_3FeCy_6 on warming. When warmed with concentrated HNO_3 or H_2SO_4 the O is liberated, largely in the form of ozone. With HCl, Cl is evolved.

Absolute alcohol has not any action on *solid* KSO_4. It dehydrates $Ba(SO_4)_2,4H_2O$, probably forming $Ba(SO_4)_2,H_2O$. It is interesting to note here another similarity to the perchlorates, for barium perchlorate crystallises with 4 mols. of water, of which 3 can be easily removed, while the last cannot be abstracted without decomposition of the salt. It is probable that the lead persulphate, like the perchlorate, crystallises with 3 molecules of water of crystallisation. The persulphates of lead and zinc are deliquescent and very readily decomposed.

Literature.—Berthelot, C. R. 86, 20, 71, and 277; 112, 1418. M. Traube, B. 22, 1518; C. J. Abs. 1889, 940; B. 24, 1764; C. J. Abs. 1891, 987. Mendeléeff, Bl. 38, 168. H. Marshall, Proc. Roy. Soc. Edin., 18, 63; C. J. 1891, 771. Richarz, B. 21, 1670; C. J. Abs. 1888, 12 and 769.

SUMAC. The commercial sumac is obtained from the various species of *Rhus*, such as *Rhus Coriaria*, *Rhus Cotinus*, *Rhus glabra*, *Rhus canadensis*, *Rhus typhina*, *Rhus pentaphylla*, and *Rhus uva ursi*. The principal species sold in the European markets, and most valued, are the Sicilian sumac (*Rhus Coriaria*), and that from Central Italy (*Rhus Cotinus* and *Rhus Coriaria*), which plants are not only collected in Central Italy but also in Dalmatia, Istria, and Montenegro, and are commercially known as Fiume sumac. Besides, there is Spanish sumac and French sumac. Of the latter, four brands are distinguished, which, however, belong all either to *Rhus Coriaria myrtifolia* or *Rhus pen-*

taphylla, according to the regions where found, as Fauvis sumac (Département du Var), Redoul sumac (Gironde), Pudis sumac (South France), and Dongère sumac (Rhone). Finally, American sumac is obtained from various species of rhus, the best being that derived from *Rhus glabra*, *Rhus canadensis*, and *Rhus typhina*. More recently another tannin-bearing plant is often offered in the market as sumac under the name of Swedish sumac. Although of very inferior quality, this product, obtained from *Arbutus uva ursi* and *Vaccinium Vitis*, is fraudulently sold for sumac, the deception being easy to carry out, as both leaves and twigs of these plants very much resemble those of the various species of rhus. Only a close examination shows the difference.

The principal value of sumac consists in the proportion of real tannin which it contains, or rather a tannic acid which, though not identical with the tannic acid of nutgalls, produces reactions similar to those of the latter, or possesses similar properties. The quantity of dyestuff contained in sumac plays in practice only a subordinate part.

It seems that there are several tannic acids contained in sumac, some of which resemble the tannic acids of nutgalls (tannin), while the others are similar to gallotannic acid. The former are designated as actual value in tannin of sumac, the latter give the so-called gallotannic value. Only the tannin contained in sumac is of actual value to the tanner and dyer, because this class of tannic acid compounds alone has the property of forming insoluble salts with metallic oxides, and thus serving for the fixation of mordants, and as a mordant for aniline and other dyestuffs. About the value of gallotannic acid in dyeing, opinions are greatly divided.

The tannic acids readily soluble in water are pretty completely precipitated from their solutions by various reagents, as by sulphuric acid, many salts, and solution of glue. Of all these reagents, however, only the solution of glue has been adopted for practical use, according to the proposition of Meunier and Warrington, who invented a method of determining tannin by titration. This method was declared insufficient by G. Müller, who demonstrated that an exact quantitative analysis by this process is impossible, as the precipitate formed does not perfectly separate out, and the solution remaining turbid prevents the observation of the end of the reaction. Although an addition of alum in some degree removes this difficulty, this method, despite all modifications added to it by Müller, F. Schulze, and others, remains inaccurate. Loewe showed that many tannic-acid-bearing materials, sumac included, contain besides it other substances soluble in water, which act like tannin, and thereby render the correctness of the analysis problematical.

Since the method of precipitating tannic acid with glue has been shown to be invalid, attention has been directed to the use of metallic salts capable of precipitating tannic acids as insoluble precipitates, and H. Fleck pointed out the property of acetate of copper of completely precipitating tannic acid as well as gallotannic acid. Since cupric gallotannate is perfectly soluble in a solution of ammonium carbonate, while cupric tannate is insoluble in this re-agent, the road towards exact examination again seemed to have been found. But this method was also condemned by many chemists, and although modified by Eder, Hayer, and others, it has been finally rejected as insufficient.

Hardtke introduced ferric acetate instead of the cupric salt as precipitating agent, but this method of titration, as well as that of Gerland (with solution of tartar emetic), proved inaccurate. Hammer's method is based upon the property of tanning materials to give insoluble precipitates with animal skin. Although Hammer's original process was very complex, it gave, in combination with other methods, the basis for the exact determination of the tannins.

A considerable step towards improvement was taken by Löwenthal. This chemist based his method upon the oxidisability of the tannins by potassium permanganate or chloride of lime, using a surplus of indigo carmine as indicator. This method, combined with that of Hammer, forms at present the principal basis of all determinations of tannin, and the improvements introduced in the combined (or, as it is called, improved) method of Löwenthal only concern the way of proceeding, but not its principles (S. C. I. 1884, 82 and 524; also 1885, 263).

In order, now, to determine the value in tannin, a certain quantity of the substance to be examined is weighed off, say 5 grms. sumac, perfectly extracted with boiling water, and the decoction made up to 1 litre. For the test, 20 c.c. of the decoction are placed in a beaker, and 750 c.c. distilled water, 10 c.c. of 1·10 normal sulphuric acid, and 20 c.c. solution of indigo carmine (of known percentage), and manganate of potash (3 litres water and 4 grms. $KMnO_4$), is introduced from a burette until the original blue colour of the solution to be titrated is changed to straw yellow. According to the quantity of solution of permanganate the total value in tannin and gallotannic acid is then calculated. It is an error to believe that the tannin of sumac is identical with the tannin of nutgalls or of other tanner's plants. On the contrary, nearly every tannin-bearing plant has a specific tannin of its own, which resembles the tannic acid of nutgalls only in the properties of giving with certain metallic salts precipitates which are insoluble in water, and of tanning the animal skins to be precipitated by the latter.

It was found that from the yield of extract of a certain kind of sumac no conclusion as to its value in tannin can be drawn. While a yield of 30 to 40 p.c. extract is by no means a rare occurrence, no sumac was discovered that contained over 25 p.c. actual tannin. Good sumac averages 10–15 p.c. actual tannin, its value in extract ranging from 30–40 p.c. It is, therefore, a great mistake if, for the valuation of a given kind of sumac, simply a decoction of it with a certain quantity of water is made, its specific gravity found, and the estimation of the value of the test-sumac made accordingly. This method may have special value for the extract-maker, but to the dyer and tanner it affords absolutely no reliable indication of the value of the article; and yet this method of valuation is practically applied in many dye-houses and tanneries.

In the commercial sumacs, besides sand and yellow earth (loam), sometimes up to 15 p.c. spent tanning barks of inferior value, such as chestnutwood, quebracho wood, quercitron bark and waste of fustic, are found as adulterants. As regards the latter two adulterations, it seems that their object is to produce the colour peculiar to the concomitant dye-stuff which is contained in sumac, especially when the sumac in question either naturally contains but little of this accompanying dye-stuff, or when its colour has been degraded by other additions or by fermentation of the leaves in a damp store. But as the principal value of sumac, not to say its only value, depends upon its content of tannin, the additions of other colouring bodies appears to be a useless waste of the latter. Sand and loam go mostly together with waste of chestnutwood used for adulteration; probably the tannin contained in chestnut wood (which, besides, is about 50 p.c. cheaper than sumac) is to compensate the deficiency in tannin which is produced by the admixture of loam and sand. What trouble such admixture of another tannic-acid-bearing material together with a dark-colouring companion dye-stuff may cause the dyer, anyone may judge by contrasting a dye with chestnut or quebracho with a sumac dye (S. C. I. 9, 607).

SUMBUL OLEO-RESIN *v.* Oleo-resins.

SUMBULAMIC ACID *v.* Oleo-resins.

SUNFLOWER OIL *v.* Oils, fixed.

SUN GOLD *v.* Naphthalene.

SUNSTONE *v.* Felspar.

SUN YELLOW. The sodium salt of azoxystilbene disulphonic acid *v.* Azoxy-colouring matters.

SUPERPHOSPHATES *v.* Manures.

SYLVANITE *v.* Tellurium.

SYLVIC ACID. Impure abietic acid *v.* *Colophony*, art. Resins.

SYLVINE. Native potassium chloride *v.* Potassium.

SYNANTHROSE or **LEVULIN** $C_6H_{10}O_5$. An isomeride of inulin found together with that body in the dahlia and Jerusalem artichoke. Found also on young rye grain and in oak bark. An amorphous deliquescent body, of a sweet taste, and converted by warming with dilute acids into dextrose and levulose. Solution optically inactive, and without action on Fehling's solution.

SYNGERITE *v.* Calcium.

SYNTONIN *v.* Albuminoids.

SZMIKITE. Native monohydrated manganous sulphate $MnSO_4.H_2O$ (Schröckinger, J. M. 1877, 729).

T

TACAMAHAC, *Tacamahacin* *v.* Oleo-resins.

TACHYDRITE $CaCl_2.2MgCl_2.12H_2O$. A mineral occurring in the salt deposits of Stassfürt in roundish, yellow, deliquescent masses.

TAGUA NUT. The fruit of *Phytelephas macrocarpa*, worked as 'vegetable ivory.'

TA-HONG. A lead glass containing ferric oxide, used by the Chinese as a red enamel on porcelain.

TAIGU WOOD. A wood from Paraguay, resembling guaiacum wood in appearance. Has a greenish-brown colour when fresh; becomes covered on exposure to the air with a greenish-yellow crystalline powder; and exhibits under the microscope yellow oblique prisms, together with shining, colourless, thin six-sided tables. The latter are not altered by alkalis; the former, which consist of *taiguic acid*, are reddened thereby. Strong boiling alcohol extracts from it 13·7 p.c. of a mixture of taiguic acid with resinous and waxy substances. Taiguic acid $(C_4H_4O)_n$ crystallises in oblique prisms of a bright-yellow colour; is tasteless and odourless; m.p. 135°, and sublimes at 180°. Very slightly soluble in water, except under pressure; readily soluble in acetone, ether, benzene, and strong alcohol. Forms crystallisable salts with bases; those with the alkalis are deep red and easily soluble in water, the lead salt is yellow, and the silver salt cinnabar-coloured (Arnaudon, J. 1858, 264).

TALC. A hydrated magnesium silicate, identical in composition with steatite, but distinctly crystalline in structure. It usually occurs in plates, apparently belonging to the orthorhombic system, and presenting a perfect basal cleavage, like that of mica. It differs, however, from mica in that the laminæ, though flexible, are not elastic. The mineral often presents a pearly lustre; and, like steatite, is unctuous to the touch. It is so soft as to be readily scratched by the finger-nail.

The applications of talc in the arts are much the same as those of steatite. When ground, it is employed as a lubricating agent, while the fibrous kinds have found extensive use in paper-mills, especially in America, where talc has largely replaced china-clay as an economical 'filler.' The high glaze of certain American papers is attributed to the admixture of talc with the pulp. A sample from New Jersey, known commercially as *agalite*, was analysed by W. Ivison Macadam with the following result: SiO_2, 62·077; MgO, 33·126; FeO, 0·104; Al_2O_3, 0·313; H_2O, 4·286 (Min. Mag. 7, 1886, 75). G. F. Perrenoud has described (Min. Res. U. S., 1886) the talc of St. Lawrence Co., New York, which, when ground, is sold to paper-makers under the names of agalite, mineral pulp, asbestine pulp, &c.

The chemical constitution of talc has been discussed by F. W. Clarke and E. A. Schneider (Ber. 23, 1537; S. C. I. 9, 970). Their experiments were made with talc from Hunter's Mill, Virginia, which when dried in air yielded SiO_2, 62·27 p.c.; Al_2O_3, 0·15; Fe_2O_3, 0·95; MgO, 30·95; FeO, 0·85; loss on ignition, 4·84. These figures agree closely with the empirical formula for talc, $H_2Mg_3Si_4O_{12}$. Whilst the mineral is generally regarded as an acid meta-silicate, $H_2Mg_3(SiO_3)_4$, Groth has viewed it rather as a basic pyrosilicate, $Mg(Si_2O_5)_2(MgOH)_2$, derived from the acid $H_2Si_2O_5$. Talc is scarcely attacked by aqueous hydrochloric acid, and this behaviour, not less than the reaction of the mineral when heated, leads Clarke and Schneider to doubt the validity of Groth's view. On the alteration of quartz into talc and steatite at Göpfersgrün, in the Fichtelgebirge, *v.* E. Weinschenk in Zeit. Kryst. Min. 14, 1888, 305 (*v.* also French chalk; Steatite). F. W. R.

TALLINGITE $CuCl_2.4Cu.H_2O_2.4H_2O$ (Church, C. J. 18, 77). A copper oxychloride found in the Botallack mine, Cornwall. Forms greenish-blue spherules. H = 3. Sp. gr. 3·5. Insoluble in water, soluble in dilute acids and in ammonia. Closely allied to *atacamite* and *botallackite*.

TALLOW (*Suif*, Fr.; *Talg*, Ger.). The term 'tallow' is principally applied to the mixture of olein and stearin obtained by rendering beef or mutton fat. Various vegetable fats, the grease obtained by boiling or steaming bones, the solids obtained by expression of whale and fish oil, and certain other solid fats are, however, also known as varieties of tallow.

Inferior kinds of animal tallow used for soap-making are known as 'melted stuff,' 'rough stuff' and 'town tallow,' the latter being also known as 'kitchen stuff' or 'pot grease,' and consisting of the waste obtained in cooking operations. Varieties whose name depends on the place of export are known as 'River Plate,' 'North American' and 'Western Tallow,' the two latter coming from the United States.

So important is the tallow industry, that in South America and Australia immense numbers of cattle were formerly slaughtered and boiled down for their tallow alone.

The following table shows in hundredweights our imports of tallow and stearin during the years 1886-1888:—

	1886	1887	1888
Russia . . .	35,579	6,532	11,434
Australia . .	—	416,658	550,495
Argentine Republic	—	22,209	80,147
United States .	—	329,367	311,022
Total imports .	1,010,396	895,658	1,146,070

Fig. 1 shows an arrangement employed by Dale, of Bristol, for rendering fat. It consists of a strong iron cylinder having a charging hole *b*, a manhole near the bottom for discharging the refuse, taps *c* for drawing off the fat, water supply valves *d*, steam supply valves *e*, and a waste valve *f*. The charge is heated by steam supplied at 60-80 lbs. pressure, and circulating through the coil *g*, beneath a perforated bottom supporting the fat, and water is supplied at *d* when necessary. After six or eight hours the tallow may be drawn off, alone or with water, by opening the upper or lower tap *c*.

At the East London Soap Works, the fresh, thoroughly disintegrated beef-suet is laid in thin layers on shallow iron trays placed in rows on inclined racks, arranged on each side of a large wooden chamber, and sloping towards a central passage therein. An open gutter leads from the lower edge of each row of trays to an external receiver. The temperature is raised by steam pipes until the fat just runs out into the receiver.

Fig. 2 shows one of a series of cylinders of 1,200 to 1,500 gallons capacity, employed in rendering the fats when the tissues are not required in a condition otherwise than is suitable for manure. The cylinders are filled above a false bottom with the crude fat, and steam is admitted by a foot valve and perforated pipe at 50 to 70, or even as high as 100, lbs. pressure. A cock is opened to allow escape of condensed water, when spurting occurs on opening a try-

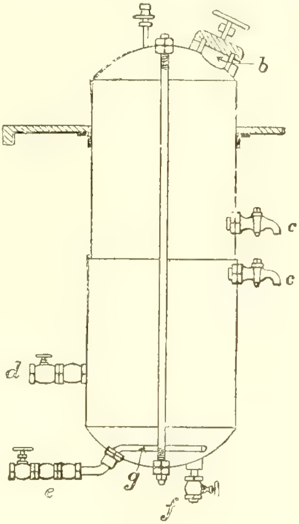


Fig. 1.

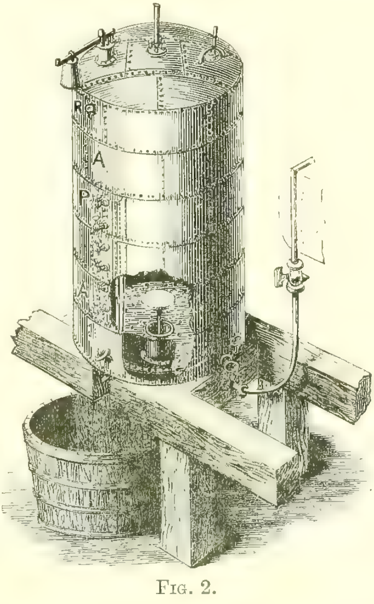


Fig. 2.

cock R. After ten to fifteen hours the steam is cut off, and the cock R and safety-valve are opened, and, after settling, the layer of tallow is drawn off through a series of cocks *p*. The cover of a discharge hole in the bottom of the cylinder is then raised by a rod, and the residual tissue falls into the tub beneath. The tallow requires to be washed, melted, and strained, to remove the last traces of tissue. This process extracts more tallow from the fat than any other.

Sometimes the fat is rendered at the atmospheric pressure by boiling a mixture of the fat with one-fourth its bulk of water containing 2 p.c. to 3 p.c. of sulphuric acid.

The quality of tallow varies with the species, age, and sex of the animal, and with the part of the body from which it is obtained. Animals fed on brewery refuse usually yield a tallow containing a lower proportion of stearin. Mutton tallow contains the largest proportion of stearin, and is whiter than beef tallow.

Tallow consists principally of stearin, olein, and palmitin, the two former largely predominating. Pure tallow is white and almost tasteless, but the commercial product is usually yellowish. It dissolves in about 40 parts of boiling alcohol of sp.gr. 0·82, and has at 15–16° a sp. gr. of 0·925–0·929 for beef tallow, and 0·937–0·940 for mutton tallow. When saponified, it yields about 94–95 p.c. of fatty acids.

Tallow melts between 100 and 120°F., the best varieties melting at about 110°. It may be distilled in vacuo (Schuller, A. Ch. [2] 18, 317), but is decomposed when distilled with superheated steam, into oleic, stearic, and palmitic acids, with separation of glycerin. Its iodine equivalent is very low, the absorption varying between 40° and 41°, and by determining this constant, adulteration with cotton-seed oil, whose iodine equivalent is relatively high, may be readily detected (Rowland Williams, S. C. I. 1888, 186).

When exposed to the air, tallow becomes whiter, and, owing to its disagreeable smell and the discoloured soap which it produces, is known as 'foxy tallow.'

Commercial tallow frequently contains a considerable quantity of free fatty acid, and is often adulterated with cotton-seed stearin, bone-fat, the distilled fatty acids from wool-grease, and other fats more fusible than stearin. Starch, china clay, and whiting are also used as adulterants. Deering (S. C. I. 3, 540) has found only one sample of tallow free from acid out of twenty-five examined, the acidity ranging from 0·85 p.c. in a sample of Australian mutton tallow to 12·20 p.c. in a Russian tallow. L. Meyer (D. P. J. 247, 305) has examined a sample of tallow consisting almost entirely of fatty acids from wool-grease, and yielding only 0·2 p.c. of glycerin.

A number of vegetable tallows are now used in considerable quantity, either alone or, more usually, with other tallows, in the soap and candle industry (*v.* Lach, Chem. Zeit. 1885, 951). They contain about 95 p.c. of saponifiable matter, of which stearin constitutes a larger proportion than in tallow.

A variety known as 'Chinese tallow,' or 'Minjak Tengkawang,' is obtained from the tallow tree or *Stillingia sebifera*, which is indigenous to China, but is also grown in Borneo, India, and America. The fruit or nut is a black, globular case containing three ovoid seeds coated with a thick, hard tallow, which constitutes 20 or 30 p.c. of the fruit, and inclosing a liquid fat. When the fruit falls from the tree it is gathered and steeped in water for thirty days, after which it is steamed for ten or fifteen minutes, washed in large mortars, and heated in bamboo sieves, where the tallow passes off as a brown liquid. This is placed in superimposed circles of twisted straw bound together to form a cylinder, and fitted in a press, and is expressed while still liquid, and allowed to cool and solidify. Sometimes the tallow surrounding the nuts is separated before extraction of the inclosed oil.

Chinese tallow melts between 35° and 42°C., and contains free fatty acids to the extent of 9·5 to 10 p.c., calculated as stearic acid. When fresh it has a pale-green colour, which changes to yellow, and finally white, on exposure to the air (*v.* also Geitel, J. pr. 36, 515; Bakker, Ph. [3] 15, 407 and 428, and the Seifenseid. Zeitung, 35, 415).

'Piney' tallow or 'veratria fat' is obtained from the seeds of the *Veratria indica* of the East Indies. These seeds contain about 49 p.c. of a solid, greenish-yellow, balsamic-smelling fat, which whitens on exposure to light. It melts at about 40°C., and saponifies easily.

Another variety, known as 'Malayan' vegetable tallow, is obtained from various species of *Hopea* in Borneo, Java, and elsewhere. The ripe fruit, which is about the size of a walnut, is allowed to partly germinate, and is then sun-dried, shelled, and steamed in a bamboo basket, after which it is expressed through cloths and run into lengths of bamboo.

Cocoa-butter and other similar fats may also be considered as vegetable tallows.

Several processes are in use for bleaching and purifying tallow and stearin, in addition to the mechanical methods of subsidence and of filtration under pressure from a head of the liquefied tallow.

By A. Dunn's process (Pat. No. 9,682, 1843) tallow for soap-making is bleached by driving air through it in finely-divided streams while heated to 82–93°C. With an ordinary tallow the treatment occupies from ten to fifteen hours. The tallow is sometimes agitated with potassium carbonate, and allowed to settle before treatment.

It may also be bleached by boiling with a solution of bleaching powder in the proportion of 1 p.c., or of potassium chlorate in the proportion of less than 0·3 p.c. of the tallow, with addition of hydrochloric or sulphuric acid. A mixture of manganese dioxide and hydrochloric or sulphuric acid may also be used.

Tallow is said to be largely bleached by the following process (C. C. 1884, 912). It is partly saponified by heating with soda and salt solution, and the upper and lower saponified layers are drawn off for making curd soap; the middle, unsaponified portion being filtered through linen, heated to boiling with a $2\frac{1}{2}$–3 p.c. solution of alum for fifteen minutes, and left for three to five hours. It is then again heated to 170°–200°C. to complete the bleaching, care being taken to arrest the heat if any unpleasant smell is observed. The fat treated by this process should not be rancid, neither should it be too fresh.

According to Watt's process (Pat. No. 7,028, 1836), which is largely employed for bleaching palm-oil, a mixture of 25 lbs. of potassium bichromate and 60 lbs. of hydrochloric acid is heated with a ton of the fat. Watt claims the use of certain other oxidising agents.

Watson (Pat. No. 9,396, 1842) describes a method of purifying in which the melted fat is agitated at 150-212° with a solution of potassium permanganate with sufficient dilute sulphuric acid to render the whole distinctly acid. After an hour the liquid is settled and the fat is drawn off and re-melted in water.

Stearic acid may be bleached by agitation with 5 p.c. of sulphuric acid diluted with 10 p.c. of water. After settling and removal of the acid water with the aid of washing, purification may be completed by stirring in water containing the whites of twenty-five eggs to each 100 lbs. of stearin, and heating by steam. The albumen rises as a scum containing most of the mechanical impurities.

TALMI GOLD. An alloy of 86·4 p.c. copper, 12·2 p.c. zinc, 1·1 p.c. tin, and 0·3 p.c. iron, used in the manufacture of trinkets.

TA-LOU. A Chinese term for a glass flux used for enamelling on porcelain. Consists mainly of a silicate of lead containing a small quantity of copper (Ebelmen and Salvétat, A. Ch. [3] 35, 344).

TAMARITE. *Chalcophyllite*

$Cu_3As_2O_8.5CuH_2O_2 + H_2O$.

A hydrated basic copper arsenate found near Redruth (in Cornwall) and in Saxony and Hungary. Occurs in rhombohedral crystals of an emerald- or grass-green colour. $H = 2$; sp.gr. 2·4–2·66.

TAMBAC or **TOMBAC.** *White copper.* An alloy of 85 p.c. copper and 15 p.c. zinc.

TANGHIN or **TANGUIN.** The celebrated judicial poison used by the inhabitants of Madagascar has been examined by Arnaud. It was known that the toxical principle was contained in the almonds of the *Tanghinia venenifera*, belonging to the family of the *Apocynaceæ*. The almonds contain about 75 p.c. of fatty matter which could not be got rid of by simple pressing. By treating with bisulphide of carbon, however, which does not take up the tanghinin, the fat was extracted. Subsequent boiling with strong alcohol, and evaporation, yield a crystalline substance of powerful toxic properties. It has a strong action upon the heart, resembling strophanthin and ouabaïne (S. C. I. 1889, 211; 1888, 765), having, however, a more general convulsive action than these bodies.

Tanghinin forms colourless, rhombic, anhydrous crystals which melt at 182°C., and are very difficultly soluble in water, but easily in strong alcohol. It is lævorotatory, and has the following composition: Carbon, 65·74; hydrogen, 8·19; oxygen, 26·07 (Arnaud, C. R. 108, 1255–1258; S. C. I. 8, 1008).

TANNASPIDIC ACID *v.* Filix mas.

TANNENITE. A bismuth copper sulphide $Cu_2S.Bi_2S_3$, found in the Erzgebirge and near Copiapo, in long tin-white needles (Domeyko, Ann. M. [6] 5, 453).

TANNIC ACIDS, TANNINS (*Acides tanniques*, Fr.; *Gerbstoffe*, Ger.). These terms have been applied to a large class of substances which occur in many plants, and are distinguished by the following characters: they have an astringent taste; give a blue-black or a green colouration with ferric salts; are precipitated by a solution of gelatin, by albumin, and by alkaloids; unite with hide to form leather; reduce solutions of the noble metals; absorb oxygen from the air, especially in the presence of alkalis &c. All these properties are not common to every tannin, but they are more or less characteristic of the majority of them.

It was formerly believed that only one tannin existed, and it was assumed that the difference in properties of tannin from different sources was due to the presence of foreign matters. Further investigation, however, established the fact that tannins from different sources differed both in composition and in properties. One of the most characteristic differences noticed was that some tannins gave a blue or blue-black colour-reaction with ferric salts, whilst others gave a green colouration with the same reagent, and this led to a division of the tannins into the two groups of (1) iron-blueing; and (2) iron-greening tannins, and this classification is still frequently made use of. It was also assumed that those tannins which gave the blue colour-reaction, such as gallotannic acid, were derived from pyrogallol, and those giving the green colour-reaction, such as catechutannic acid, from catechol, and these two phenols were in fact obtained from certain members of the two classes of tannins by fusion with potash or by dry distillation (Watts, B. 10, 1764). Schiff (B. 15, 2590) likewise regarded the iron-blueing tannins as anhydro- compounds derived from gallic acid and those giving the green reaction as similarly derived from protocatechuic acid, his conclusions being founded partly at least on results obtained with his synthetic tannins. A classification depending upon the colour-reactions mentioned cannot, however, be regarded as scientific. Catechol derivatives are, in fact, known which give a blue colour-reaction with ferric salts, and quercitannic acid may be mentioned as an example of a tannin which yields *catechol* and protocatechuic acid on fusion with potash, but gives a *blue* colour-reaction with ferric chloride.

Stenhouse (Pr. 11, 405) believed that there was a connection between the glucoside character of some of the tannins and their colour-reactions —namely, that those tannins which give blue-black precipitates with ferric salts are mostly glucosides, a view which is now known to be erroneous. In fact, it has been shown that some of the tannins which were formerly held to be glucosides are not glucosides at all, but that the sugar accompanying them was obtained from some other plant constituent.

Wagner (Fr. 5, 1) made a distinction between *pathological* and *physiological* tannins, and maintained that the former class, represented by gallotannic acid, is only known to exist in pathological formations of certain species of oak and sumac (*Rhus javanica* and *Rh. semialata*), whilst the latter class includes all tannins which are produced under normal conditions of plant life. Pathological tannin is distinguished by the readiness with which it can be hydrolised, with formation of gallic acid; it is precipitated by gelatin, but will not convert hide into a true leather. The physiological tannins, on the other hand, include those employed by the tanner, and occur in the bark and other parts of plants. They are distinguished from pathological tannin in that they cannot be hydrolysed either by a ferment or by boiling with dilute acids. It would appear, however, that gallotannic acid does exist in some plants as a physiological tannin, as for, instance, in myrobalans and in pomegranate; and should further investigation prove this to be the case, Wagner's distinction must necessarily fall through. At the same time, the chemical properties of gallotannic acid clearly distinguish it from the true *tanning* tannins, nearly all of which, however, have been very imperfectly investigated. Of these latter, quercitannic acid has received most attention, and Etti (M. 4, 522) has shown it to be a hydroxy- derivative of ketonic acid containing the grouping $C_6H_5.CO.C_6H_4.COOH$, whilst gallotannic acid (*q. v.*) is known to be a hydroxy-derivative of $C_6H_5.CO.O.C_6H_4.COOH$, and thus the difference in properties is readily explained. On comparing the properties of the so-called physiological tannins, a large proportion of them will be seen to be closely related to quercitannic acid, and it would appear more than probable that many at least are built up on the same type as the latter. Other tannins, again, such as caffetannic acid, are glucosides.

Böttinger (B. 17, 1123) has examined the action of bromine on several tannins, and has shown that these may be grouped according to the amount of bromine which they take up; the filtered tannin extracts are agitated with a slight excess of bromine and the precipitated bromo- derivatives filtered off, washed, and dried at the atmospheric temperature. The following table gives the sources of the tannins examined and the percentages of bromine in the bromo-products formed:

Oak-bark tannin	28·4
Hemlock-bark tannin	43·6
Quebracho-wood tannin	44·5
Mangrove-bark tannin	42·15
Mimosa tannin	49·36
Chestnut oak tannin	50·48
Terra japonica tannin	53·2
Spruce bark tannin	52·8

Böttinger has also shown that tannin extracts react with phenylhydrazine, yielding amorphous products, but the reaction is complicated by the presence of saccharine substances and the mixed products have not been fully investigated (A. 246, 127; 256, 341; 259, 125). Attempts to obtain cyanhydrines and oximes were unsuccessful (A. 259, 132).

It will be seen from what has been said above, and still more clearly from a glance at the following account of the different tannins, that our knowledge of this class of substances is far too imperfect to allow of any satisfactory classification, and accordingly an alphabetical arrangement has been adopted.

Alder-tannin $C_{27}H_{28}O_{11}$ is contained in the wood of *Alnus glutinosa*; the sawdust is exhausted with boiling water, the extract treated with lead acetate, and the precipitate obtained is well washed and then decomposed by hydrogen sulphide. The greater part of the tannin is carried down with the lead sulphide, and is extracted from the latter with boiling 90 p.c. alcohol. Alder-tannin is a reddish-brown substance, is insoluble in ether, benzene, and carbon bisulphide, dissolves sparingly in absolute alcohol, more readily in boiling water, and is very readily soluble in dilute alcohol. It reduces ammonical silver solution, gives a precipitate with gelatin solution, and a dirty-green precipitate with ferric chloride.

When alder-tannin is boiled with dilute sulphuric acid it undergoes hydrolysis, a sugar $C_6H_{12}O_6$ and *alder-red* being produced. The latter, after being dried at 130°, has the composition $C_{46}H_{38}O_{13}$. Alder-red is insoluble in water and in ether, is sparingly soluble in alcohol, and dissolves in alkalis to a bright red-brown solution.

Alder-tannin yields catechol on dry distillation, and protocatechuic acid, phloroglucinol, and acetic acid when it is fused with potash.

The red colour which alder-wood acquires on exposure to air is probably due to alder-red produced by the action of a ferment on the tannin (Dreykorn and Reichard, D. P. J. 195, 157).

Algarobilla contains, according to Zölffel (Ar. Ph. 229, 123), two tannins, one of which is the *glucoside of gallotannic acid*, and is present to the extent of 8 to 10 p.c., whilst the main tanning principle is *ellagotannic acid* $C_{14}H_{10}O_{10}$ (*q. v.*), and is present in much larger quantity.

Algarobilla is used for tanning; according to Godeffroy (C. N. 40, 144), the pods contain 68·38 p.c. tannin. According to Eitner (D. P. J. 244, 80), algarobilla contains 40–50 p.c. tannin.

Anacahuita wood and **bark** contain a tannin which gives a green colour-reaction with iron salts, and which can be extracted by cold water or by alcohol (Buchner, J. 1861, 771).

Ash-tannin *v. Fraxitannic acid.*

Aspertannic acid $C_{14}H_{16}O_8$ was obtained by Schwarz (Sitz. B. 6, 446) from woodruff (*Asperula odorata*). It gives a green colouration with ferric salts, but does not give precipitates with albumin, gelatin, or tartar-emetic solutions. It is decomposed by boiling with dilute sulphuric acid, but no sugar appears to be formed, and no precipitate is produced.

Atherosperma-tannin. The bark of *Atherosperma Moschatum* contains a tannin which gives a green colouration with ferric salts. It may be precipitated by lead acetate from the clarified decoction of the bark, and on digesting the well-washed precipitate with acetic acid, filtering, and neutralising the solution with ammonia, a greyish-yellow precipitate is formed which when dried has the composition $C_{10}H_{14}PbO_3$ (Zeyer, J. 1861, 769).

Bablah contains gallic and tannic acids, *v.* vol. i. 263.

Beech-tannin. The bark of the red beech contains a tannin of the composition $C_{20}H_{22}O_9$ (Etti, M. 10, 650).

Caffetannic acid $C_{15}H_{18}O_8$ (?) occurs in coffee berries in the form of calcium and magnesium salts (Rochleder, A. 59, 300), and in cainca-root, *Chirococca racemosa* (Rochleder and Hlasiwetz, Sitz. B. 5, 6).

According to Rochleder (A. 66, 39), it is also present in Paraguay tea, *Ilex paraguayensis*, but this has been disputed by others (J. 1856, 815; Arata, J. 1877, 938). It is prepared by exhausting the coffee berries with alcohol, diluting the extract with twice its volume of water to precipitate fat, then boiling the filtrate and adding lead acetate; the precipitate is suspended in alcohol, decomposed by hydrogen sulphide, and the solution filtered and evaporated (Rochleder).

Caffetannic acid is readily soluble in water and in alcohol; it has an astringent taste, gives a dark-green colouration with ferric chloride, and reduces silver solution. It is not precipitated by gelatin or by tartar-emetic, but it gives a precipitate with salts of quinine. Its ammoniacal solution becomes green on exposure to air through absorption of oxygen and formation of viridic acid. Caffetannic acid yields catechol on dry distillation and protocatechuic acid on fusion with potash. When it is boiled with potash solution it is decomposed into caffeic acid and a sugar $C_6H_{10}O_4$ (?) (Hlasiwetz, A. 142, 220). *Viridic acid* is also present in coffee berries in the form of calcium salt (Rochleder, A. 63, 197), and is produced by the atmospheric oxidation of an ammoniacal solution of caffetannic acid; the green solution obtained is neutralised by acetic acid and lead acetate added, when a blue precipitate of lead viridate is obtained. See also Rochleder, A. 82, 196; Sitz. B. 24, 39; Payen, A. Ch. [3] 26, 108; Liebich, A. 71, 57; Pfaff, S. 62, 31; Vlaanderen and Mulder, J. 1858, 261.

Callutannic acid $C_{14}H_{14}O_9$ is contained in the common ling, *Calluna vulgaris*. The plant (without the root) is extracted with alcohol; this is then distilled off, the residue mixed with water, and the solution obtained precipitated with lead acetate. The precipitate is treated with very dilute acetic acid, filtered, the solution treated hot with basic lead acetate, the precipitate decomposed by hydrogen sulphide, and the solution thus obtained evaporated in a current of carbon dioxide.

Callutannic acid is an amber-coloured substance. It gives a green colouration with ferric chloride, and when it is heated with dilute mineral acids it yields a yellow amorphous anhydro- derivative $C_{14}H_{10}O_7$, which is soluble in hot, but nearly insoluble in cold, water (Rochleder, A. 84, 354; Sitz. B. 9, 286).

Catechutannic acid *v.* vol. i. 447

Cherry-bark tannin. According to Rochleder (Sitz. B. 59, 819) the bark of *Cerasus aceda* contains a tannin of the composition $C_{21}H_{20}O_{10}+\frac{1}{2}H_2O$. In order to obtain it, the decoction of the bark is first treated with zinc acetate, which throws down *fuscophlobaphen*, a brown amorphous substance of the composition $C_{27}H_{26}O_{12}$. On adding lead acetate to the filtrate, the lead salt of the *tannin* is precipitated together with *rubrophlobaphen* $C_{32}H_{34}O_{17}$(?), a brick-red substance which can be dissolved and separated from the tannin precipitate by acetic acid. The tannin $C_{21}H_{20}O_{10}+\frac{1}{2}H_2O$, obtained by decomposing its lead salt with hydrogen sulphide, gives a green colouration with ferric chloride. It is not a glucoside, but when its solution is heated with dilute acids an insoluble red product $C_{21}H_{16}O_8+\frac{3}{4}H_2O$ is produced.

Fuscophlobaphen appears to be a glucoside, dilute acids decomposing it with formation of a brick-red product $C_{21}H_{18}O_8+\frac{1}{2}H_2O$ and a carbohydrate. When it is fused with potash it yields formic, acetic, propionic, oxalic, and protocatechuic acids.

Rubrophlobaphen is decomposed by mineral acids, with formation of protocatechuic acid and a nearly insoluble red substance $C_{21}H_{22}O_9+\frac{1}{4}H_2O$.

Cinchonatannic acid *v. Quinotannic acid.*

Cinchona-red *v. Quinotannic acid.*

Cocatannic acid $C_{17}H_{22}O_{10}+2H_2O$(?) is present in the leaves of *Erythroxylon Coca*, from which it can be extracted by boiling water; the cocaïne which is also present in the decoction is precipitated by the addition of sodium carbonate (Niemann, J. 1860, 368). Warden (Ph. 18, 985) extracted the leaves with 90 p.c. alcohol containing one-sixtieth of its weight of sulphuric acid, and obtained cocatannic acid after purification in microscopic filiform crystals of a sulphur-yellow colour, odourless and practically tasteless. It is very sparingly soluble in cold water, absolute alcohol, ether, and chloroform; readily soluble in boiling water. It gives precipitates with lead acetate, tartar-emetic, and egg-albumin, but not with gelatin. It reduces gold and silver solutions, gives no reaction with ferrous, but a green colouration with ferric, salts.

Cortepinitannic acid occurs, together with pinicortannic acid, in the bark of the Scotch fir, *Pinus sylvestris*. For its separation see *Pinicortannic acid.* It is a bright red powder of the composition $C_{32}H_{34}O_{17}(=2C_{16}H_{11}O_7+3H_2O)$; its aqueous solution gives an intense green colouration with ferric chloride (Kawalier, Sitz. B. 11, 363).

Divi-divi *v.* vol. i. 698. Divi-divi contains ellagotannic acid (*q. v.*) $C_{14}H_{10}O_{10}$ (Löwe, Fr. 14, 35), and gallic acid (Stenhouse, A. 45, 16).

Ellagic acid *v.* vol. ii. 6.

Ellagotannic acid $C_{14}H_{10}O_{10}$ occurs in divi-divi (Löwe, Fr. 14, 35), in algarobilla (Zölffel, Ar. Ph. 229, 123), and in myrobalans (Löwe, *l.c.* 44; Zölffel, *l.c.*). Löwe obtained it from divi-divi by repeated extraction with cold alcohol; the latter is then distilled off, the residue mixed with water, filtered, and the ellagotannic acid precipitated by the addition of salt. He describes it as a brownish amorphous mass. When it is heated with water at 110° it breaks up into ellagic acid and water. The molecule of ellagotannic acid contains five hydroxyl groups replaceable by acetyl; its constitution is represented by Zölffel (*l.c.*) as

$$C_6H_2(OH)_3.CO.O.O.C_6H_2(OH)_2.COOH.$$

Ellagotannic acid gives precipitates with gelatin, albumin, alkaloids, tartar-emetic, and a nearly black precipitate with ferric acetate (Löwe). Its alcoholic solution is precipitated by lead acetate, and the lead salt obtained has the composition $2C_{14}H_{10}O_{10}.5PbO$.

Euphrasia-tannin. According to Enz, the green parts *Euphrasia officinalis* contain a tannin which gives a green colour-reaction with ferric salts. Its lead salt has the composition $C_{32}H_{20}Pb_3O_{20}$ (Vierteljahrsch. Ph. 8, 175).

Filitannic acid *v.* Filix Mas, vol. ii. 138.

Fragarianin *v. Strawberry tannin.*

Fraxitannic acid $C_{26}H_{32}O_{14}$ is one of the chief constituents of an aqueous decoction of the leaves of the ash tree, *Fraxinus excelsior.* In order to obtain it, the solution is precipitated with lead acetate, and the precipitate treated with boiling 10 p.c. acetic acid, which dissolves the lead fraxitannate. The solution is then fractionally precipitated with ammonia, the purest fractions decomposed by hydrogen sulphide, and the solution evaporated to dryness in a vacuum over sulphuric acid; the residue is extracted with absolute alcohol in a closed flask filled with carbon dioxide, the solution is distilled in a current of the same gas, the residue dissolved in water, and the solution filtered and then evaporated in a vacuum. The product forms a golden-yellow deliquescent powder; it has a rough, bitter taste, and its solution feebly reddens litmus. Sulphuric acid, hydrochloric acid, and sodium chloride precipitate it from its moderately-concentrated solutions. Tartar-emetic gives no precipitate, ferric chloride gives a dark-green colouration and precipitate, and normal lead acetate gives a golden-yellow precipitate with aqueous solutions of the acid. Fraxitannic acid reduces Fehling's solution, but it does not yield glucose when heated with dilute acids or baryta-water. When heated at 100° it loses water and forms an almost insoluble anhydride $C_{26}H_{30}O_{13}$ (Gintl and Reinitzer, M. 3, 745).

Gintl and Reinitzer have also described an *acetyl derivative* $C_{13}H_{14}(OC_2H_3O)_2O_5$, the corresponding *benzoyl derivative*, and a *bromacetyl compound* of the composition

$$C_{26}H_{25}(OC_2H_3O)_4Br_3O_{10} + 2H_2O,$$

from which it is concluded that fraxitannic acid contains four hydroxyl groups. When a solution of fraxitannic acid is repeatedly evaporated in an open vessel, a brown substance $C_{63}H_{72}O_{27}$ is produced, which is insoluble in water but soluble in absolute alcohol, and reacts like fraxitannic acid with ferric chloride and Fehling's solution. Its benzoyl derivative has the composition $C_{63}H_{66}(C_7H_5O)_6O_{27}$.

The small residue insoluble in absolute alcohol, which is left during the purification of fraxitannic acid (*v. supra*), is a lustrous brown-black friable substance readily soluble in water. Its composition is $C_{13}H_{16}O_8$. Its solution gives a brown-green precipitate with lead acetate, and a dirty brown-green precipitate with ferric chloride.

Fustic *v.* vol. ii. 173.

Galitannic acid $C_{14}H_{16}O_{10} + H_2O$ is the name given to a tannin occurring in the bark of *Galium verum* (Schwarz, A. 83, 57). It has a bitter astringent taste, gives a chrome-yellow precipitate with basic lead acetate, and a dark-green colour-reaction with ferric chloride.

Gallotannic acid, tannic acid, or **tannin** $C_{14}H_{10}O_9$, occurs in the gallnuts of various species of oak, in Chinese and Turkish gallnuts, and in certain kinds of sumac (*q. v.*). Berzelius was the first to obtain it in a state approaching purity (Lehrb. 3 Aufl. 6, 213). It was held, however, by the earlier experimenters to be a glucoside, and in accordance with this view Strecker (A. 81, 247; 90, 340) proposed the formula $C_{27}H_{22}O_{17}$. Rochleder and Kawalier subsequently showed that the amount of glucose obtainable from it varied with the degree of purity of the tannin, and by very careful purification they succeeded in reducing the yield of sugar to about 5 p.c. (J. pr. 74, 28 and 399), whilst Strecker's formula required 29·1 p.c. Schiff finally established the true nature and constitution of gallotannic acid (A. 170, 43), and accounted for the origin of the glucose by assuming that gallotannic acid exists in the gallnuts in the form of a very unstable glucoside, so unstable that it becomes hydrolysed during the process of extraction. Schiff showed that gallotannic acid has the constitution

$$C_6H_2(OH)_3CO.O.C_6H_2(OH)_2COOH,$$

this being proved by the following considerations: (1) that it possesses marked acid properties; (2) that it yields a pentacetyl derivative when heated with acetic anhydride; (3) that it can be readily and quantitively hydrolysed with formation of gallic acid; and (4) that a substance exhibiting the properties of, and probably identical with, gallotannic acid can be obtained by the action of arsenic acid or phosphorus oxychloride on gallic acid (Schiff, *l.c.*; Löwe, Z. 1868, 603). Compare also Seguin, A. Ch. 20, 15; Berzelius, *ibid.* 94, 318; Lehrb. 3 Aufl. 6, 213; Gmelin-Krant; Pelouze, A. Ch. 54, 337; Liebig, A. 10, 172; Büchner, A. 53, 175; Stenhouse, P. M. 1843, 417; Wetherill, J. Ph. [3] 12, 107; Mulder, A. 31, 124; Freda, G. 1878, 9.

Preparation.—See vol. ii. 302.

Properties.—Gallotannic acid is an almost colourless, amorphous substance, which becomes yellow when exposed to light. It is inodorous, has a strongly astringent taste, dissolves readily in water and in alcohol, is almost insoluble in pure anhydrous ether, whilst in ether containing water it dissolves with separation of a dense and mainly aqueous solution, the upper ethereal layer containing but little tannic acid. It is soluble also in acetone, in glycerin, and in the fixed and volatile oils; it is insoluble in carbon bisulphide, chloroform, petroleum, and benzene. Its aqueous solution reddens litmus, decomposes carbonates, and gives a blue-black colouration and precipitate with ferric salts; it gives precipitates also with tartar-emetic, with the alkaloids, with gelatin, albumin, and starch solutions. The gelatin precipitate contains 16·5 p.c. nitrogen, which corresponds with 34 p.c. tannin (Böttinger, A. 244, 227). Gallotannic acid is also precipitated from its solutions by a number of salts, such as sodium chloride, ammonium chloride, potassium sulphate, potassium acetate, and others, and also by sulphuric acid and hydrochloric acid, but not by potassium nitrate or sodium sulphate (Strecker, A. 90, 361).

Gallotannic acid is precipitated by lead acetate, and as the lead gallotannate is insoluble in dilute acetic acid whilst lead gallate is insoluble, Guyard (Bl. 41, 337) proposed the use of these reagents for distinguishing and separating gallic and gallotannic acids. According to Spence (S. C. I. 1890, 1114), however, here is very little difference in solubility, and he one cannot be dissolved without the other.

When gallotannic acid is heated to 150–160°, it darkens in colour, and at 215° it decomposes, yielding pyrogallol, carbon dioxide, and a trace of metagallic acid $C_6H_4O_2$; if, however, it be heated rapidly to 240–250°, metagallic acid is produced without pyrogallol, water being also formed (Pelouze, A. 10, 159). When a dilute solution of gallotannic acid is exposed to the air, it becomes discoloured, oxygen is absorbed, whilst gallic acid and carbon dioxide are produced. Guyard (Bl. 41, 336) has shown, however, that air purified by being passed through a series of tubes containing potash solution, cotton-wool, soda-lime, and calcium chloride has no action on a solution of tannin, and concludes that the decomposition mentioned is, therefore, in all probability due to atmospheric particles or ferments which possibly act without the co-operation of oxygen. Ozonised air oxidises gallotannic acid with formation of oxalic acid (Gorup-Besanez, A. 110, 86); cold dilute nitric acid oxidises it to carbon dioxide, oxalic acid, and other products, amongst which appear to be trihydroxyglutaric and trihydroxybutyric acids (Böttinger, A. 257, 248). Gallotannic acid reduces silver carbonate to metal, and solutions of ferric, cupric, and mercuric salts to the ferrous, cuprous, and mercurous condition. It reduces Fehling's solution, 1 grm. cupric oxide corresponding with 0·4126 grm. tannin (Sonnenschein, D. P. J. 256, 555). In the presence of alkali, gallotannic acid becomes rapidly oxidised by atmospheric oxygen. When it is boiled with potash solution (sp. gr. 1·27), the potash being kept in slight excess, *tannomelanic acid* $C_6H_4O_3$ is produced, but when gallotannic acid is dissolved in cold caustic potash solution and exposed to the air for three or four days at the atmospheric temperature, *tannoxylic acid* $C_7H_6O_6$ is formed (Büchner, A. 53, 373; Gerhardt's 'Traité,' 3, 874).

When gallotannic acid is boiled with dilute sulphuric acid it becomes hydrolysed, and gallic acid is produced:

$$C_6H_2(OH)_3CO.O.C_6H_2(OH)_2.COOH + H_2O = \\ 2C_6H_2(OH)_3COOH$$

and the same decomposition can be effected by boiling with dilute alkali or by the action of a ferment, *Penicillium glaucum* or *Aspergillus niger* (van Tieghem, C. R. 65, 1092).

When gallotannic acid is boiled with acetic anhydride, it becomes converted into its pentacetyl derivative

$$C_6H_2(OC_2H_3O)_3CO.O.C_6H_2(OC_2H_3O)_2COOH,$$

a crystalline substance which melts at 137°; it gives no colour-reaction with iron salts (Schiff, *l.c.*, 72; Böttinger, B. 17, 1504).

When dilute solutions of tannin and iodine are mixed, a colourless liquid is obtained which forms a very delicate test for alkalis, with which it gives a red colouration. The colouration is perceptible with a solution containing one part of potassium carbonate in 1,000,000 (Griessmayer, Fr. 11, 43; Schweissinger, C. N. 51, 114).

Salts.—Gallotannic acid forms normal and basic salts, a number of which have been prepared. Compare Büchner, A. 53, 361; Gerland, C. N. 8, 54; Cap, Viertelj. Ph. 8, 589; Harff, Ph. C. 1836, 350; Helm, Viertelj. Ph. 11, 99; Mulder, R. P. [3] 1, 311, 2, 38; Schiff, A. 175, 168; 104, 327; Strecker, A. 90, 347; Pelouze, A. 10, 153; Pavesi and Rotondi, B. 7, 590; Willstein, R. P. 95, 289.

Uses.—Gallotannic acid is employed in the preparation of gallic acid and pyrogallol; it is used also in medicine, in the preparation of ink, and as a mordant in dyeing. It is also recommended for clarifying sugar solutions (Germ. Pat. 1886, 39,279).

Hemlock-tannin $C_{20}H_{18}O_{10}$. Hemlock-bark extract is prepared on a very large scale in North America for tanning purposes. The tannin contained in it appears to be related to quercitannic acid $C_{19}H_{16}O_{10}$, and is regarded by Böttinger as a homologue of the latter. When the tannin solution is heated for some time with concentrated hydrochloric acid, or with sulphuric acid, an anhydride, *hemlock-red* $C_{40}H_{30}O_{17}$ separates, forming a red powder; it is insoluble in water, alcohol, and ether, but dissolves in cold dilute caustic soda and in warm sodium carbonate solution. On heating hemlock-red with concentrated hydrochloric acid at 180°, a black product is obtained, whilst methyl chloride, carbon dioxide, and water are given off. When heated with acetic anhydride, hemlock-red is converted into a brownish-yellow acetyl derivative $C_{40}H_{23}(C_2H_3O)_7O_{17}$ insoluble in water, alcohol, and acetic ether. A mixture of two bromine derivatives $C_{40}H_{20}Br_{10}O_{17}$ and $C_{40}H_{16}Br_{14}O_{17}$ is obtained by the action of bromine on hemlock-red suspended in chloroform, and these are separated by means of ether, which dissolves the higher bromination product only. An ethyl-derivative obtained by heating hemlock-red with ethyl iodide and alcoholic potash at 130° is insoluble in dilute caustic soda, but dissolves readily in alcohol (Böttinger, B. 17, 1125). When bromine is added to the diluted tannin extract a *tetrabromo- derivative* $C_{20}H_{14}Br_4O_{10}$ is thrown down as a yellow precipitate readily soluble in alcohol, acetic ether, and glacial acetic acid, very readily also in acetone and in acetic anhydride, but is insoluble in chloroform and in carbon bisulphide. Alkalis and their carbonates dissolve it, forming brown solutions. Tetrabromo-hemlock-tannin behaves like hemlock-red when heated with hydrochloric acid; when heated with acetic anhydride it yields a tetrabromo-pentacetyl derivative $C_{20}H_9(C_2H_3O)_5Br_4O_{10}$, and when suspended in chloroform and treated with bromine it gives a hexabromo- compound $C_{20}H_{10}Br_6O_{10}$ (B. 17, 1041).

Hop-tannin is prepared as follows. The hops are extracted first with ether, then with absolute alcohol to remove resin, wax, and chlorophyl, and finally with 70 p.c. alcohol (by volume). On adding lead acetate to this extract, phlobaphen is first precipitated and is separated; the tannin is then thrown down by the further addition of lead acetate, and the precipitate is decomposed by hydrogen sulphide. Hop-tannin is readily soluble in water, in dilute alcohol, and in acetic ether, less soluble in absolute alcohol, and insoluble in ether. Its aqueous solution gives a precipitate with albumin, but does not precipitate either gelatin or tartar-emetic; it can be precipitated by sodium chloride and by mineral acids. It gives a dark-green colouration with ferric chloride, reduces alkaline copper solutions, and gives a yellow precipitate with lead acetate. *Hop-phlobaphen* $C_{50}H_{46}O_{25}$, obtained from the first lead acetate precipitate mentioned (*v. supra*), is a black-red substance somewhat soluble in boiling water, readily in alkalis, and sparingly in dilute mineral acids. Boiling dilute sulphuric acid hydrolyses it, with formation of glucose and *hop-red* $C_{38}H_{26}O_{15}$.

Hop-red forms a cinnamon-coloured powder, which on fusion with potash yields phloroglucinol and protocatechuic acid; its alkaline solution does not reduce Fehling's solution (Etti, A. 180, 223).

According to a more recent statement of Etti's (M. 10, 651), hop-tannin has the composition $C_{22}H_{26}O_9$.

Horsechestnut-tannin $C_{26}H_{24}O_{12}$ is present in nearly all parts of the tree *Æsculus Hippocastanum*, and in the root-bark of the apple-tree (Rochleder, Sitz. B. 53 [2] 478; 54 [2] 609). It is an amorphous nearly colourless substance, having a strongly astringent taste, is readily soluble in water, alcohol, and in ether. Its solution gives an intense green colouration with ferric chloride, which changes to violet on adding an alkali; it is precipitated by gelatin, but not by tartar-emetic. When it is heated with dilute mineral acids, the solution becomes red and a cinnabar-coloured substance separates; this has the composition $C_{26}H_{22}O_{11}$ or $C_{26}H_{20}O_{10}$, according to the strength of acid used. The compound $C_{26}H_{20}O_{10}$ exists in two modifications, one soluble and the other insoluble in alcohol.

When horsechestnut-tannin is heated at 127° it becomes converted into a greyish substance of the composition $C_{26}H_{22}O_{11}$, but which differs from the substance of the same composition obtained by the action of an acid in that it cannot be reconverted into the original tannin by boiling with water. Horsechestnut-tannin is completely precipitated by aluminium hydrate; it is precipitated also by lead acetate, and the precipitate is soluble in dilute acetic acid. On fusion with potash, phloroglucinol and protocatechuic acid are produced. *V.* also *Phyllæscitannin.*

Ipecacuanhic acid $C_{14}H_{18}O_7$ was obtained by Willigt (A. 76, 342) from the roots of *Cephalis Ipecacuanha* by extraction with boiling alcohol, and was isolated by means of its lead salt. It is a reddish-brown, very bitter, amorphous, and very hygroscopic substance, soluble in water, alcohol, and in ether. Its solution gives a green colouration with ferric chloride.

Kino *v.* vol. ii. 386.

Larch-tannin. The bark of the larch contains considerable quantities of a tannin, which was examined by Stenhouse (P. M. 23, 336). Larch-tannin gives a precipitate with gelatin, but not with tartar-emetic. It gives an olive-green precipitate with ferric salts. When it is boiled with sulphuric acid no sugar is produced; the scarlet solution which is obtained deposits red flocks, sparingly soluble in cold water but readily soluble in alcohol and in alkalis, forming rich scarlet solutions.

Leditannic acid *v.* vol. ii. 458.

Maclurin *v.* FUSTIC.

Mangrove-bark contains a tannin which gives a green colour-reaction with ferric chloride, and which yields a brownish-red amorphous precipitate when it is boiled with dilute sulphuric acid. It is not a glucoside (Stenhouse, Pr. 11, 405).

Morin *v.* FUSTIC.

Myrobalans were shown by Stenhouse (P. M. 23, 334) to contain gallic acid and a tannin, differing from gallotannic acid. Löwe (Fr. 14, 44) showed this to be ellagotannic acid $C_{14}H_{10}O_{10}$, identical with the tannin contained in divi-divi. According to Zölffel (Ar. Ph. 229, 123), myrobalans contains mainly ellagotannic acid, but also, in smaller quantity, a glucoside of gallotannic acid and some gallic acid.

The glucoside present yields glucose and gallic acid on hydrolysis.

Myrobalans are used for tanning and for the production of a black dye.

Nucitannic acid occurs, together with gallic and ellagic acids, in the episperm of the walnut (Phipson, C. N. 20, 116). It is soluble in water and in alcohol, can be precipitated by lead acetate, and is resolved, by boiling with dilute acids, into glucose and a brownish-red amorphous substance, *rothic acid* $C_{14}H_{12}O_7$, which separates as the liquid cools. Rothic acid is readily soluble in alcohol and in ammonia.

Œnotannin was obtained by Gautier from red wine (Bl. 27, 496). The wine is carefully neutralised with sodium carbonate, ammonium chloride added to precipitate colouring matter, and the filtrate digested with freshly-precipitated copper carbonate; on decomposing the copper precipitate with hydrogen sulphide, œnotannin is obtained. It is a colourless substance, soluble in water, alcohol, and in ether. It gives a green precipitate with ferric chloride, is imperfectly precipitated by gelatin; it reduces hot ammoniacal silver solution, but does not reduce Fehling's solution. When œnotannin is exposed to moist air, it becomes converted into an insoluble red-coloured substance, which is probably related to the colouring matter of red wine.

Oxypinitannic acid *v.* *Pinitannic acid.*

Phyllæscitannin $C_{26}H_{24}O_{13},H_2O$ is the name given by Rochleder (Z. 1867, 84) to a tannin present in the small leaflets of the horsechestnut as long as they remain inclosed in the buds. In order to obtain it, the alcohol extract of the leaflets is treated with lead acetate, the precipitate digested with dilute acetic acid, and the undissolved residue decomposed by hydrogen sulphide. Phyllæscitannin is an amorphous reddish-brown substance, having a strongly astringent taste.

Pinicortannic acid and **cortepinitannic acid** occur in the bark of the Scotch fir, *Pinus sylvestris.* The bark, gathered in winter from old trees, is extracted with alcohol, the solution concentrated, allowed to cool, and filtered from a wax-like substance which separates. The greater portion of the alcohol is then distilled off, and the residue mixed with water. On adding lead acetate to the solution, lead pinicortannate is precipitated, whilst cortepinitannic acid still remains in solution, and can be precipitated by the addition of basic lead acetate. The lead pinicortannate is dissolved in dilute acetic acid, filtered, thrown down with basic lead acetate, and the precipitate decomposed by hydrogen sulphide. The solution of pinicortannic acid is evaporated in a current of carbon dioxide, and the product dried in a vacuum. It forms a reddish-brown powder, of the composition

$$C_{32}H_{38}O_{23} = 2C_{16}H_{18}O_{11} + H_2O.$$

After it has been dried it dissolves very sparingly in water. When it is boiled with dilute hydrochloric acid it becomes dehydrated and converted into a bright-red compound $C_{48}H_{50}O_{31}$ $(= 3C_{16}H_{16}O_{10} + H_2O)$. The solution of pinicortannic acid gives a green colouration with ferric chloride (Kawalier, Sitz. B. 11, 361). See also *Cortepinitannic acid.*

Pinitannic acid $C_{14}H_{16}O_8$, and **Oxypinitannic acid** $C_{14}H_{16}O_9$, occur in the needles of the Scotch fir, *Pinus sylvestris* (Kawalier, Sitz. B. 11, 356). The needles are exhausted with alcohol, the extract evaporated, and the residue treated with water, which throws down some resinous matter; a few drops of a solution of lead acetate are added to aid clarification, and, after filtration, an excess of the same reagent is added to precipitate the *oxypinitannic acid.* The filtrate from this is heated to the boiling-point, and the pinitannic acid thrown down by the addition of basic lead acetate. Pinitannic acid is also present in the green parts of the common arbor vitæ, *Thuja occidentalis* (Rochleder, Sitz. B. 29, 20). It is a reddish-yellow substance, of the composition $C_{14}H_{16}O_8$, is readily soluble in water, alcohol, and ether; it does not precipitate either gelatin or tartar-emetic, but gives a yellow precipitate with lead acetate, readily soluble in dilute acetic acid, and a dark red-brown colouration with ferric chloride. It reduces ammoniacal silver solution. When it is boiled with dilute acids, it yields a sparingly-soluble red product and a substance which reduces alkaline copper solutions (Rochleder and Kawalier, Sitz. B. 29, 21).

Oxypinitannic acid is a brownish-grey substance, readily soluble in water and in alcohol. It has a very astringent taste. Its solution gives an intense green colouration with ferric chloride, a lemon-yellow precipitate with lead acetate, and is not precipitated by gelatin or tartar-emetic; reduces hot ammoniacal silver solution. When it is boiled with dilute hydrochloric acid, the solution acquires a carmine colour, and when treated with concentrated sulphuric acid a red solution is obtained, which gives a flocculent precipitate on the addition of water (Kawalier, Sitz. B. 11, 356).

Pomegranate-tannin $C_{20}H_{16}O_{13}$ is a glucoside contained in the root-bark of *Punica Granatum.* On adding basic lead acetate to an aqueous decoction of the bark, gallotannic acid is first precipitated and then the above-mentioned tannin. Pomegranate-tannin is an amorphous, greenish-yellow substance, having an astringent taste. It is insoluble in alcohol and in ether; it reduces silver solution and Fehling's solution, is precipitated by gelatin and by tartar-emetic, and gives a black precipitate with ferric salts. Boiling dilute sulphuric acid hydrolyses it, with formation of a sugar $C_6H_{12}O_6$, and ellagic acid (Rembold, A. 143, 285).

Pteritannic acid *v.* FILIX MAS.

Quebrachitannic acid may be obtained from the gum or from the wood of *Quebracho colorado.* The purified gum is dissolved in boiling water and the solution filtered and left to cool, when the tannin will be deposited in reddish tufts and should be quickly filtered off, pressed, and dried over sulphuric acid. It is a pale-red amorphous substance, having an astringent taste. It is precipitated from its aqueous solution by various salts, and it also yields precipitates with lead acetate, tartar-emetic, gelatin, albumin, and the alkaloids; it gives a green colouration with ferric chloride. Quebrachitannic acid yields catechol on dry distillation, and phloroglucinol and protocatechuic acid on fusion with potash. Strong nitric acid oxidises it to oxalic and picric acids. According to Arata, quebrachitannic acid contains 52·52 p.c. carbon and 5·11 p.c. hydrogen (Arata, Anales de la Sociedad Cientifica Argentina, Feb. 1879; Jean, Bl. 28, 16).

When bromine is added to the tannin extract prepared from quebracho wood, a bromine derivative is obtained containing 44·5 p.c. bromine. This bromo-tannin, dissolved in alcohol, reacts with hydroxylamine hydrochloride. When it is heated with concentrated hydrochloric acid at 189–190° it yields a black product, whilst hydrobromic acid, carbon dioxide, and a gas which burns with a green flame (methyl chloride ?) are evolved (Böttinger, B. 17, 1124).

Quercitannic acid is found in the bark, wood, and leaves of the oak, and is said to be present also in tea (*q. v.*). It was first shown by Stenhouse to differ from gallotannic acid (P. M. 22, 425). According to Etti (M. 10, 650), quercitannic acid is present in the oak mainly in the form of a very soluble salt (probably magnesium salt), and is best prepared from the commercial extract which is manufactured for tanners. The extract is diluted with water, allowed to settle, and filtered. Concentrated hydrochloric acid is added to the filtrate as long as a precipitate is produced, and this is separated, well washed, dried. dissolved in 95 p.c. alcohol, and the solution filtered and mixed with $1\frac{1}{4}$ times its volume of water. The filtrate from the black precipitate which is produced is evaporated to dryness, and if the residue is completely soluble in spirit of 40–45° it is regarded as pure. Compare also Böttinger, A. 202, 270; Löwe, Fr. 20, 210; Etti, M. 1, 264.

Quercitannic acid was formerly held to be a glucoside (Grabowski, Sitz. B. 56 [2] 388; Oser, *ibid.* 72 [2] 178; Johansen, Ar. Ph. [3] 9, 210; Böttinger, B. 14, 1598), but Etti showed that the pure substance did not yield a trace of sugar, and he attributed the error to an impurity of levulin, which is present in oak bark (B. 14, 1826; M. 4, 512). *V.* also Löwe, Fr. 20, 208.

Various formulæ have been assigned to quercitannic acid, namely: $C_{20}H_{20}O_{11}$ (Oser, *l.c.*), $C_{28}H_{30}O_{15}$ (Löwe, *l.c.*), $C_{19}H_{16}O_{10}$ (Böttinger, B. 16, 2712), $C_{15}H_{12}O_9 + 2H_2O$—contained in oak wood (*ibid.* B. 20, 761), $C_{17}H_{16}O_9$, $C_{18}H_{18}O_9$, and $C_{20}H_{20}O_9$—from different species of oak bark (Etti, M. 10, 650), and $C_{14}H_{14}O_9$—from oak wood (*ibid. l.c.*); and although it is most improbable that each of these formulæ represents a distinct substance, it would appear from Etti's researches that the same quercitannic acid is not present in all oaks. The tannin $C_{17}H_{16}O_9$ obtained from *Quercus robur* gives a blue colour-reaction with ferric chloride, whilst that, $O_{20}H_{20}O_9$, obtained from *Q. pubescens* gives a grass-green colouration and precipitate with the same reagent. In other respects, however, the different quercitannic acids behave very much alike, and are no doubt similarly constituted (Etti, B. 17, 1823; M. 1, 525).

Quercitannic acid is described by Etti as a reddish-white powder, readily soluble in dilute alcohol, less so in ethyl acetate, and sparingly soluble in cold water. It gives a pale-yellow precipitate with lead acetate, and is precipitated also by gelatin, albumin, tartar-emetic, and the alkaloids. One of its most characteristic properties is the readiness with which it forms sparingly-soluble reddish-brown anhydrides when heated either by itself or with dilute acids (*v. infra*). When quercitannic acid is heated with dilute sulphuric acid at 130-140° in a sealed tube it yields about 1·5 p.c. gallic acid, whilst the greater portion is converted into anhydrides (Etti, B. 17, 184); when it is heated with concentrated hydrochloric acid at 150–180° a little gallic acid is also produced, together with oak-red and some methyl chloride (*ibid.* M. 1, 274), and when it is boiled with acetic anhydride acetyl derivatives of its anhydrides are produced. On dry distillation it yields small quantities of dimethylcatechol, catechol, and a product not identified; and on fusion with potash it gives protocatechuic acid, catechol, and traces of phloroglucinol.

By the action of bromine on aqueous oak bark extract, Böttinger obtained a *dibromoquercitannic acid* $C_{19}H_{14}Br_2O_{10}$ as a yellow precipitate, sparingly soluble in water, moderately in alcohol and in acetic ether, but very soluble in a mixture of the last two solvents, and readily also in dilute alkalis. When it is heated (not above 80°) with acetic anhydrides it yields *pentacetyldibromoquercitannic acid* $C_{19}H_5(C_2H_3O)_5Br_2O_{10}$, and when heated with concentrated hydrochloric acid at 180°, methyl chloride, carbon dioxide, hydrogen chloride, and water are liberated, whilst a black product $(C_{17}H_5O_6)_x$(?) is obtained. Dibromoquercitannic acid reacts with hydroxylamine hydrochloride, forming $C_{19}H_{15}Br_2NO_{10}$. When it is suspended in chloroform and further brominated it yields *tetrabromodehydroquercitannic acid* $C_{19}H_{10}Br_4O_{10}$.

Quercitannic acids from oak wood. Böttinger obtained an oak-wood tannin

$$C_{15}H_{12}O_9 + 2H_2O$$

by heating the crude tannin with acetic anhydride, and afterwards decomposing the acetyl derivative formed by heating it with water at 135°. It is a light yellowish-brown substance, readily soluble in water. Its aqueous solution gives a pale-yellow precipitate with lead acetate, a white flocculent precipitate with gelatine, but no precipitate with bromine. It loses 1 molecule H_2O at 100°, and the second molecule at 135°. Etti's oak-wood tannin $C_{16}H_{14}O_9$, obtained from the extract by precipitation with hydrochloric acid (M. 10, 651), is, on the other hand, a brownish-red amorphous substance practically insoluble in water and in absolute ether, and very readily soluble in alcohol and in acetone. It gives a yellowish-white precipitate with lead acetate, reacts with phenylhydrazine, forming a yellow amorphous hydrazone $C_{22}H_{20}N_2O_8$, and with hydroxylamine forming a brown amorphous oxime $C_{16}H_{15}NO_9$. When it is heated with dilute sulphuric acid at 120–130° it yields insoluble anhydrides and some gallic acid. It contains two methoxyl groups, but only one methyl group can be removed by boiling with hydriodic acid or by heating with hydrochloric acid; the product $C_{15}H_{12}O_9$ from the last reaction can, however, be proved by Zeisel's method to still contain methoxyl, and it is concluded, therefore, that the quercitannic acid $C_{16}H_{14}O_9$ is a dimethyl derivative of $C_{14}H_{10}O_9$.

The production of a small quantity of gallic acid on heating quercitannic acid with dilute acids, and the formation of a hydrazone and an oxime, have led Etti to conclude that quercitannic acid is derived from a ketonic acid $C_6H_2(OH)_3.CO.C_6H(OH)_3.COOH$, in which the hydroxyl groups occupy the same position as in gallic acid, and the oak-wood tannin $C_{16}H_{14}O_9$ is regarded as the dimethyl derivative of this ketonic acid.

By the action of sodium-amalgam on the acetyl derivative of *oak-wood tannin*, Böttinger (A. 263, 108) has obtained the following products: *Hydroquercic acid* $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_8$; *querlactone* $C_5H_6O_2$, an acid which is probably *trihydroxybutyric acid*, a substance not yet identified, and which very readily undergoes oxidation; also acetic, oxalic, and quercitannic acids, and traces of gallic acid. *Hydroquercic acid* is a greyish-brown hygroscopic substance, has a bitter taste, is appreciably soluble in boiling water, and readily in alcohol. Its *acetyl derivative* $C_{15}H_{14}(C_2H_3O)_2O_6$ is a brownish-grey powder; its *barium salt* forms a voluminous amorphous precipitate which, when dried at 100°, has the composition $(C_{15}H_{15}O_6)_2Ba$; and its *lead salt* has the composition $(C_{15}H_{15}O_6)_2Pb$. *Querlactone* melts in boiling water, in which it is but sparingly soluble; it is readily soluble in acetic acid, alcohol, ether, and ethyl acetate. It reduces ammoniacal silver nitrate; its lead salt has the composition $(C_5H_7O_3)_2Pb$.

When *oak-bark tannin* is treated with sodium-amalgam, *hydroquercic acid* is also obtained, together with *hydroquergalic acid*, *lagic acid* $C_4H_4O_3$, identical with the substance obtained by the oxidation of gallic acid, trihydroxybutyric acid, and a little gallic acid. *Hydroquergalic acid* $C_{14}H_{14}O_6$ is a brownish-red amorphous substance readily soluble in boiling water, sparingly in cold water, and insoluble in alcohol, ether, ethyl acetate, acetic anhydride, and acetic acid.

Anhydrides. The terms *phlobaphen* and *oak-red* have been applied—sometimes indiscriminately—to the anhydrides of quercitannic acid. Phlobaphen is, as its name implies, the coloured constituent of the bark, and appears to be identical with the anhydride obtained on heating quercitannic acid at 130° (Etti), or, according to Böttinger, with the anhydride formed when quercitannic acid is heated with dilute mineral acid (A. 202, 269). For its preparation from oak-bark, *v.* Böttinger (*ibid.* 270) and Etti (M. 1, 269). It is described by the latter chemist as a reddish-brown substance practically insoluble in water and in ether; readily soluble in alcohol. It is also soluble to a considerable extent in solution of quercitannic acid and in aqueous alkalis, forming with the latter reddish-brown solutions which absorb oxygen from the air and which reduce Fehling's solution. The composition of phlobaphen is as variously stated as that of quercitannic acid. According to Grabowski (Sitz. B. 56 [2] 390), its composition is $C_{26}H_{24}O_{14}$, whilst Böttinger (A. 240, 339) assigns to it the formula $C_{38}H_{26}O_{17}$, and Etti gives the formulæ $C_{34}H_{30}O_{17}$ and $C_{40}H_{38}O_{17}$, corresponding with the two quercitannic acids $C_{17}H_{16}O_9$ and $C_{20}H_{20}O_9$.

When phlobaphen is heated with alkyl iodides and alcoholic potash, it yields ethereal derivatives readily soluble in alcohol; heated with fuming hydrochloric acid at 180–230°, it gives carbon dioxide and a lustrous black substance $C_{36}H_{22}O_{11}$ (Böttinger, B. 16, 2711). Cold dilute nitric acid oxidises phlobaphen with production of carbon dioxide, oxalic, and other acids, apparently trihydroxyglutaric and trihydroxybutyric acids (*ibid.* A. 257, 248). According to Böttinger, phlobaphen contains seven hydroxyl groups replaceable by acetyl and benzoyl groups, but no ketonic group. The same investigator also describes a *hexabromo-* derivative $C_{38}H_{20}Br_6O_{17}$, which, when heated with acetic anhydride, yields a *hexabromo-heptacetyl-*compound $C_{38}H_{13}Br_6(C_2H_3O)_7O_{17}$, and a *decabromo-* compound obtained by the bromination of the hexabromo- derivative.

Etti states that the quercitannic acids yield as many as four different anhydrides, and the following is the series obtained from the bark-acid $C_{17}H_{16}O_9$: (1) $C_{34}H_{30}O_{17}$, obtained by heating quercitannic acid at 130–140°, is sparingly soluble in water, readily in alcohol and in alkalis, and is identical with the phlobaphen of the bark and with Grabowski's oak-red; (2) $C_{34}H_{28}O_{16}$, obtained by boiling the last with dilute sulphuric acid; (3) $C_{34}H_{26}O_{15}$ (Oser's oak-red), formed when quercitannic acid is heated with dilute sulphuric acid; (4) $C_{34}H_{24}O_{14}$ (Löwe's oak-red), obtained by heating quercitannic acid with water or dilute acid for eight days at 110° (Löwe, Fr. 20, 216). Etti's second quercitannic acid $C_{20}H_{20}O_9$ also gives four different anhydrides (M. 4, 525). The anhydrides from Etti's oakwood tannin $C_{16}H_{14}O_9$ have the composition indicated by the following formulæ: $C_{32}H_{24}O_{16}$, $C_{32}H_{20}O_{14}$, and $C_{32}H_{18}O_{13}$. The last of these differs from the others in being insoluble in alcohol and in potash; it is devoid of acid properties.

Quinotannic acid or **Cinchonatannic acid** is obtained from cinchona bark as follows: A decoction of the bark is treated with calcined magnesia, which precipitates cinchona-red, and lead acetate is added to the filtrate; the precipitate is decomposed by hydrogen sulphide, and the filtrate from the lead sulphide is precipitated with basic lead acetate. The precipitate is dissolved in dilute acetic acid, and the solution filtered from undissolved impurity. On adding ammonia to the solution, a pale-yellow lead salt is precipitated; this is again decomposed by hydrogen sulphide, and the solution of quinotannic acid is evaporated in a vacuum over sulphuric acid (Schwarz, Sitz. B. 7, 250).

Quinotannic acid is a light-yellow, very hygroscopic substance, soluble in water, alcohol, and ether; it has a slightly sour and astringent taste, gives precipitates with gelatin, tartar-emetic, albumin, starch, and a green precipitate with ferric salts. It readily absorbs oxygen from the air, and when exposed in ammoniacal solution becomes converted into cinchona-red (Schwarz, *l.c.*). It is decomposed by boiling with dilute hydrochloric or sulphuric acid, yielding a sugar and *cinchona-red* $C_{28}H_{22}O_{14}$ (Rembold, A. 143, 270), a brownish-red substance which gives protocatechuic acid and some acetic acid on fusion with potash. Cinchona-red is present in cinchona bark, and can be extracted from it by ammonia; the ammoniacal extract is acidulated with hydrochloric acid, which precipitates cinchona-red and quinovic acid. The precipitate is boiled with milk of lime, the solution of calcium quinovate filtered off, and the residue treated with warm dilute hydrochloric acid, filtered, and washed. Cinchona-red is a chocolate-brown substance, almost insoluble in water, readily soluble in alcohol, ether, and in alkalis (Schwarz). According to Schwarz, quinotannic acid has the composition $C_{14}H_{16}O_9$, and cinchona-red the composition $C_{12}H_{14}O_7$. *Cf.* also Berzelius, Lehrb. 3 Aufl. 6, 246; Pelletier a. Caventou, A. Ch. 15, 337.

Quinovatannic acid $C_{14}H_{18}O_8$ is contained in the bark of *Cinchona nova*, and in many respects resembles quinotannic acid (Hlasiwetz, A. 79, 129). It is a yellow substance, soluble in water and in alcohol, but insoluble in ether. It gives a dark-green colour-reaction with ferric chloride. When it is boiled with dilute acids it yields a sugar and *quinova-red* $C_{12}H_{12}O_5$. This is also present in the bark, from which it can be extracted by ammonia. It is an almost black resin-like substance, is almost insoluble in water, but dissolves readily in alcohol, ether, and in alkalis. On fusion with potash, it yields protocatechuic acid (Rembold. A. 143, 273).

Rhamnotannic acid was obtained by Binswanger (R. P. 104, 54) from the juice of buckthorn berries. When the juice, after being concentrated by evaporation, is exhausted with hot alcohol, and the alcoholic solution evaporated and then mixed with water, *rhamnotannic acid* is precipitated. After purification, it forms a neutral, greenish-yellow amorphous mass, having a bitter and astringent taste. It is nearly insoluble in cold water, is readily soluble in alcohol and in ether, and yields yellow solutions with ammonia, potash, and with lime-water. It gives a yellow colouration and precipitate with ferric salts; it does not precipitate gelatin.

Rhatany-tannin $C_{20}H_{20}O_9$ can be extracted from the bark of rhatany-root, *Krameria triandra* and purified by means of its lead salt (Wittstein, J. 1854, 656). Raabe (J. 1880, 1060) describes it as a light-yellow amorphous powder, readily soluble in water, alcohol, and acetic ether, and almost insoluble in pure ether. It gives a green colouration with ferric chloride, precipitates gelatin and albumin, but does not give a precipitate with tartar-emetic; it reduces gold solutions and alkaline copper solutions. When it is heated with dilute acids it yields insoluble *rhatany-red*, and according to Grabowski (A. 143, 274) also a sugar, whilst Raabe (*l.c.*) states that no sugar is produced. Grabowski assigns to rhatany-red the formula $C_{26}H_{22}O_{11}$, whilst according to Raabe its composition is $C_{20}H_{18}O_8$. When rhatany-red is fused with potash, it yields phloroglucinol and protocatechuic acid. On dry distillation it yields catechol.

The rhatany-red which is present in rhatany-root bark appears to have a different composition from the *red* just described.

Raabe's formula for rhatany-tannin is deduced from the composition of its lead and copper salts.

Rheotannic acid $C_{26}H_{26}O_{14}$ is contained in the aqueous extract of rhubarb-root, and may be separated by means of its lead salt. It forms a yellowish-brown powder, readily soluble in hot water and in alcohol. Its solution is precipitated by gelatin, albumin, and by alkaloids, but not by tartar-emetic. It yields a black-green precipitate with ferric chloride, reduces gold and silver solutions, and is resolved by boiling with dilute mineral acids into a fermentable sugar and *rheic acid* $C_{20}H_{16}O_9$. This is sparingly soluble in cold water, more readily soluble in alcohol and in hot water (Kubly, Z. 1868, 308).

Rhodotannic acid is present in the leaves of *Rhododendron ferrugineum.* The leaves are extracted with alcohol, the solution evaporated, the residue treated with water, and the solution filtered and precipitated with lead acetate. Rhodotannic acid is an amber-coloured substance having an astringent taste. When dried in a vacuum over sulphuric acid its composition agrees with the formula $4C_{14}H_{12}O_7 + 3H_2O$. Its solution gives a green colour-reaction with ferric chloride. When it is heated with dilute mineral acids, a reddish-yellow precipitate of rhodoxanthin $C_{14}H_{14}O_8$ (?) is produced (Schwarz, Sitz. B. 9, 298).

Rubitannic acid $2C_{14}H_{22}O_{12} + H_2O$ was obtained by Willigt (A. 82, 340) from the leaves of *Rubia tinctoria.* It gives a green colour-reaction with ferric chloride.

Sorbitannic acid is contained in the juice of the ripe berries of the mountain ash, *Sorbus aucuparia.* The juice is fermented to remove glucose, a little lead acetate is added, the solution filtered, and the sorbitannic acid then precipitated by the addition of an excess of lead acetate. The precipitate is washed, decomposed by hydrogen sulphide, and the solution evaporated in a vacuum; the residue is treated with absolute alcohol, and the solution again evaporated, when the sorbitannic acid is obtained as a thick syrupy mass. It gives an intense yellow colouration with alkalis, is not precipitated either by alum, gelatin, or salts of quinine; it reduces silver salts, and gives an intense dark-green colouration with ferric salts, the colour becoming reddish-brown on the addition of alkalis. When its solution is heated with dilute sulphuric acid, it becomes reddish-yellow, but no precipitate is formed. Nitric acid produces a deep-yellow colouration.

Sorbitannic acid yields catechol on dry distillation, and protocatechuic acid and phloroglucinol when it is fused with potash (Vincent and Delachanal, Bl. 47, 492).

Spruce-bark tannin $C_{21}H_{20}O_{10}$ (?). By the action of bromine on aqueous spruce-bark extract, Böttinger obtained an unstable bromo-tannin to which he assigned the formula $C_{21}H_{14}Br_6O_{10}$. This reacts with hydroxylamine hydrochloride, and when it is heated at 180–190° with concentrated hydrochloric acid it becomes decomposed, with liberation of methyl chloride, carbon dioxide, hydrogen bromide, and water. When the hexabromo- compound is treated with acetic anhydride, it yields a pentacetylpentabromo-derivative $C_{21}H_5(C_2H_3O)_5Br_5O_{10}$.

Spruce-red is produced when the bark-extract is boiled with hydrochloric or sulphuric acid, but the product, which is an insoluble anhydride of spruce-bark tannin, varies in properties with the acid employed. When hydrochloric acid is used, the product is brown and yields an acetyl derivative of the composition $C_{42}H_{27}(C_2H_3O)_7O_{17}$, whilst the product from the action of sulphuric acid is more yellowish-grey, and yields an acetyl derivative of the composition $C_{21}H_{13}(C_2H_3O)_3O_8$. When spruce-red is suspended in chloroform and brominated, a bromo-derivative of the composition $C_{42}H_{24}Br_{10}O_{17}$ is obtained (Böttinger, B. 17, 1127).

Strawberry-root contains a tannin *fragarianin*, which, according to Phipson (C. N. 38, 135), is analogous to quinotannic acid. It has a very pale-yellow colour, dissolves in water and in alcohol, and is precipitated from its aqueous solution by hydrochloric acid. It gives a green colouration with ferric chloride, and when it is boiled with hydrochloric acid it becomes hydrolysed, with formation of glucose and separation of an amorphous reddish-brown substance *fragarin.* This is somewhat soluble in water, alcohol, and ether, and dissolves in potash to a fine reddish-purple solution. On dry distillation it yields a substance which appears to be catechol, and on fusion with potash it gives a little protocatechuic acid.

Sumac consists of the dried and powdered leaves of various species of Rhus, especially *Rh. Coriaria.* The kind known as Sicilian sumac is considered the best. Löwe (Fr. 12, 128) states that the tannin of Sicilian sumac is identical with *gallotannic acid* (see also Stenhouse, A. 45, 9), whilst, according to Wagner (Fr. 5, 1), the latter is only present in two kinds of sumac—namely, those derived from *Rh. javanica* and *Rh. semialata.* Wagner states that the tannin of sumac derived from *Rh. Coriaria* and *Rh. typhina* cannot be resolved by hydrolysis into gallic acid, as is the case with gallotannic acid. According to Löwe (*l.c.*), the tannin of Tyrolese sumac appears to differ from gallotannic acid, and to be more nearly related to quercitannic acid (*v.* SUMAC).

Tannaspidic acid *v.* FILIX MAS, vol. ii.

Tannecortepinic acid $C_{28}H_{26}O_{12}$ is the name given to tannin found in the bark of young Scotch firs (twenty to twenty-five years old) collected about Easter (Rochleder a. Kawalier, Sitz. B. 29, 23). It is a reddish-brown substance, is soluble in water, and has an astringent taste; it gives a dark-green colouration with ferric chloride. When it is heated with dilute sulphuric or hydrochloric acid, it yields a red precipitate of nearly the same composition as the original substance together with a little sugar.

Tannopinic acid $C_{28}H_{30}O_{13}$ (?) is sometimes present in the needles of the Scotch fir when gathered about Easter (Rochleder and Kawalier, Sitz. B. 29, 22). In the winter-time oxypinitannic acid appears to take its place, but whether this is produced by the oxidation of the tannopinic acid, or the latter by the reduction of the oxypinitannic acid has not been determined.

Tea leaves contain *gallic acid* and *quercitannic acid* (Stenhouse, P. M. 23, 332; Rochleder, A. 63, 205; Hlasiwetz a. Malin, J. pr. 101, 109).

The amount of tannin in tea averages about 10 p.c. (Allen, C. N. 29, 189), and, according to Hooper (C. N. 60, 311), is not influenced either by the quality of the tea or by the altitude at which it is grown (*v.* TEA).

Terra japonica or **Gambier** is an extract obtained from the leaves of *Uncaria gambir.* The tannin which it contains resembles spruce-bark tannin in composition and properties, and, like the latter, it also yields an insoluble *red*, the colour and composition of which vary with the mode of preparation (*v. Spruce-bark tannin*). Two preparations of *terra japonica red* obtained by the action of hydrochloric acid of different strengths and at different temperatures yielded acetyl derivatives of the composition $C_{21}H_{14}(C_2H_3O)_4O_9$ and $C_{21}H_{14}(C_2H_3O)_3O_8$ (Böttinger, B. 17, 1129).

Tormentilla. The root of *Potentilla tormentilla* contains a *tannin* of the composition $C_{26}H_{22}O_{11}$, *tormentil-red, quinovic acid,* and a substance which yields *ellagic acid* when boiled with potash solution (Rembold, A. 145, 5). In order to obtain the tannin, lead acetate is added to the aqueous decoction of the root, and the precipitate decomposed under water by hydrogen sulphide. The tannin solution obtained is again precipitated, first with normal lead acetate, which throws down impure tannin, and then with basic acetate, and the precipitates are separately decomposed by hydrogen sulphide. The tannin obtained from the second of these precipitates forms an amorphous reddish powder of the composition $C_{26}H_{22}O_{11}$. Its solution gives a blue-green colour-reaction with ferric chloride, and yields a precipitate with gelatin. When it is boiled with dilute sulphuric acid, it yields *tormentil-red,* without any appreciable formation of sugar. Tormentil-red appears to have the same composition as tormentilla-tannin. It yields phloroglucinol and protocatechuic acid on fusion with potash.

Valonia. The commercial name given to the acorn-cups of *Quercus Ægilops* imported from the Levant. It contains 19 to 26·7 p.c. of a tannin (Wagner, Fr. 5, 10) which Stenhouse found to differ from gallotannic acid (P. M. 22, 424), it also contains a little gallic acid. Valonia is used for tanning leather.

Willow-bark tannin. The bark of *Salix triandra* and *S. undulata* contains a tannin which gives a green colour-reaction with ferric salts. It is a glucoside, and when boiled with dilute sulphuric acid yields a brown-red precipitate nearly insoluble in water, but soluble in alcohol and in alkalis (Stenhouse, Pr. 11, 403; Johanson, Ar. Ph. [3] 13, 103).

Xanthotannic acid. According to Ferrein (J. 1858, 463), the yellow colour of elm leaves in autumn is due to xanthotannic acid. The lead salt of this tannin has the composition $C_{28}H_{36}O_4.3PbO$.

Animal tannin. According to Villon (C. N. 56, 175), a substance showing all the general characters of tannin can be extracted from corn-weevils (*Calandra granaria*). The weevils are killed, ground in a mortar, and extracted with boiling 90 p.c. alcohol. The solution is evaporated, the residue dissolved in ethyl acetate, and the tannin precipitated by the addition of ammoniacal zinc acetate. The precipitate is decomposed by oxalic acid, and the tannin solution evaporated in a vacuum, when it is obtained in the form of reddish-yellow scales. Villon names it *fracticornitannin.*

Synthetic tannins. Löwe was the first to show that a substance possessing the properties of ordinary tannin was formed by the decomposition of silver gallate (Z. 1868, 111) or when gallic acid is heated with arsenic acid (J. pr. 103, 464). Schiff repeated and extended these experiments, and with the help of phosphorus oxychloride he obtained a product which he maintained was identical with gallotannic acid, and which, like the latter, could be readily hydrolysed, and gallic acid reproduced (A. 170, 49). He also showed that true analogues of gallotannic acid could likewise be obtained by the action of phosphorus oxychloride on other phenolcarboxylic acids, and also from phenolsulphonic acids. Thus from ordinary phenolsulphonic acid he obtained the product $C_6H_4(OH)SO_2.O.C_6H_4.SO_2OH$ (B. 5, 437), and from pyrogallolsulphonic acid he prepared $C_6H_2(OH)_3SO_2.O.C_6H_2(OH)_2SO_2OH$ (B. 5, 663), and a similar product also from phloroglucinolsulphonic acid (B. 6, 26). These synthetic tannin analogues possess an astringent taste, and their solutions yield precipitates with albumin, gelatin, alkaloids, and several acids and salts just as is the case with ordinary tannin.

From protocatechuic acid, the same chemist obtained a *diprotocatechuic acid* $C_{14}H_{10}O_7$ and a *tetraprotocatechuic acid* $C_{28}H_{18}O_{13}$, both of which exhibit the reactions of gallotannic acid, except that they give a green colour-reaction with ferric chloride (B. 15, 2588). Pyrogallol-carboxylic acid yields a *dipyrogallolcarboxylic* $C_{14}H_{10}O_9$ of very similar properties, but showing a violet colouration with ferric chloride, whilst phloroglucinolcarboxylic acid would appear to react differently with phosphorus oxychloride, and to yield a product more nearly related to the bark tannins (Schiff, A. 245, 35).

Böttinger states (B. 17, 1475) that a digallic acid isomeric with gallotannic acid and resembling the latter in many of its properties is produced when gallic acid or its ethyl salt is moistened with pyruvic or glyoxylic acid, and heated with concentrated sulphuric acid. The part played by the pyruvic acid is obscure.

According to Hunt (C. N. 52, 49), a substance showing many of the reactions characteristic of tannin is formed when potassium gallate is heated with monobromoprotocatechuic acid and alcohol.

Estimation.—For the estimation of the tannins see articles on Leather and Sumac.

TANNING *v.* Leather.

TANTALITE *v.* Niobium.

TANTALUM. Sym. Ta. At. w. 182·0 (Marignac). For the occurrence of this metal see Niobium. Tantalum is obtained as a black powder, acquiring an iron-grey lustre when burnished. It burns when heated gently in air, and ignites in chlorine or sulphur vapour. It dissolves in hydrofluoric acid, but is insoluble in all other acids, including aqua regia.

Tantalum forms two oxides, Ta_2O_4 and Ta_2O_5, one sulphide Ta_2S_4, a nitride, pentachloride, pentabromide, and in solution a pentafluoride, but no iodide.

TAP CINDER. The basic silicate of iron constituting the slag and flowing through the tap-hole of the puddling furnace, *v.* Iron.

TAPIOCA is prepared from cassava meal by moistening it and drying it in granules upon hot plates. By this treatment the starch cells swell and burst, adhering in small irregular masses. See Cassava and Manihot.

TAR, COAL, *v.* Gas, coal.

TAR, WOOD, *v.* Wood, destructive distillation of.

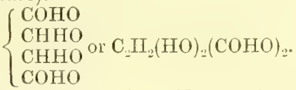
TARAXACERIN, TARAXACIN, TARAXACUM *v.* Dandelion root.

TARTAR *v.* Tartaric acid.

TARTAR, CREAM OF, *Acid potassium tartrate v.* Tartaric acid.

TARTAR EMETIC, *Potassium antimony tartrate v.* Antimony.

TARTARIC ACID, *Dihydroxy-succinic acid* (*Acide tartarique* ; *Weinsäure, Weinsteinsäure, Tartarsäure*).



$$\left\{\begin{array}{l}COHO\\CHHO\\CHHO\\COHO\end{array}\right. \text{or } C_2H_2(HO)_2(COHO)_2.$$

The existence of the acid potassium salt of this acid in the deposit from fermented grape-juice was known to the Greeks and Romans, and the term *tartarum* was applied to the deposit by Paracelsus, but it was generally considered to be an acid and to contain no base, although an alkali was known to be present in its ash. The production of an alkali by boiling tartar with lime was noticed by Kunkel in 1677, but the acid was not isolated until 1769, when Scheele (Crell's Chem. J. 2, 179) obtained it by boiling tartar with chalk and decomposing the product with sulphuric acid.

Five varieties of tartaric acid are known, viz. the ordinary or dextrotartaric acid, and lævotartaric acid, which rotate the plane of polarised light to the right and left respectively ; the optically inactive racemic acid, which can be decomposed into the above acids ; the inactive mesotartaric acid, which cannot be so decomposed; and metatartaric acid, obtained by fusion of dextrotartaric acid.

Racemic or paratartaric acid was discovered by Kestner in the mother-liquors of tartaric acid obtained from the vintage of 1822 (C. R. 29, 526, 557), and was examined by Gay-Lussac (S. 48, 381), Walchner (*ibid.* 49, 238), Berzelius (P. 19, 319), and Biot (A. Ch. [2] 69, 22), the latter of whom pointed out its optical inactivity. This was further examined by Pasteur (C. R. 36, 19, and 37, 162), who decomposed it into a mixture of dextro- and lævo- tartaric acids, whose optical activities are equal and opposite.

Racemic acid appears to exist to some extent in grape juice, but is principally produced during the fermentation. It is said to be formed in considerable quantity when tartaric acid solutions are evaporated with the acid of superheated steam or by ordinary heating, but not when evaporation is conducted in a vacuum pan (*v.* Hofmann's Ber. über die Entwickelung der Chem. Ind. ii. 423). Warington, however (C. J. 1875, 989), has found no evidence of the production of this acid in the treatment through which tartaric acid ordinarily passes in the factory. Lidow (B. 14, 2689) has found it as the calcium salt in the dye vats where bleaching powder has been treated with tartaric acid.

Racemic acid is best obtained by heating dextrotartaric acid with one-seventh to one-tenth its weight of water at 170° for about 30 hours (Jungfleisch, Bl. 18, 201). According to Dessaignes (Bl. 1863, 355), dextrotartaric acid is partly converted into racemic acid by prolonged heating at ordinary pressures with water or dilute acid. It is also obtained by oxidising fumaric acid with potassium permanganate (Kekulé a. Anschütz, B. 13, 2150 ; A. 226, 191), and, together with mesotartaric acid, when cinchonine dextro- or lævo- tartrate is heated for some time at 170° (Pasteur, C. R. 37, 162).

Racemic acid crystallises in holohedral triclinic prisms of sp.gr. $\frac{7°}{4°}$ 1·6873 (Perkin, C. J. 1887, 362) containing one molecule of water, and is somewhat less soluble in water, and much less soluble in alcohol, than dextrotartaric acid. The anhydrous acid melts at 189–201° (Städel, B. 11, 1752). The work of Perkin (*l.c.*) appears to indicate that racemic acid is almost entirely decomposed into dextro- and lævo- tartaric acids on solution. The admixture of those acids, however, caused marked evolution of heat.

The racemates closely resemble the dextrotartrates, but are of no commercial interest. The calcium salt, which crystallises in microscopic crystals containing four molecules of water (Anschütz, A. 226, 191), is less soluble than calcium dextrotartrate. Warington (C. J. 1875, 944) has observed a form of calcium racemate which separates from cold dilute undisturbed solutions in feathery crystals.

Lævo-tartaric or **anti-tartaric acid** was first obtained by Pasteur (C. R. 36, 19, and 37, 162), by crystallisation of a solution of ammonium sodium racemate obtained by mixing the two halves of a solution of racemic acid, which had been respectively neutralised with ammonium and sodium carbonate. The product was found to consist of a mixture of hemihedral crystals, some having the hemihedral faces developed to the right and others to the left, the former being dextrorotatory and the latter lævorotatory. The acid obtained from the former was found to be dextrotartaric acid, while the new lævorotatory acid obtained from the latter received the name lævotartaric acid.

This acid—which closely resembles dextrotartaric acid, but ferments less readily—occurs in anhydrous rhombic crystals. Lævotartrates generally exhibit the same properties and have the same solubilities as the dextrotartrates, but the compounds of the two acids with optically active substances, such as asparagine and optically active hydricammonic malate, as well as the salts with cinchonine, quinine, brucine, and strychnine, differ considerably (Pasteur, A. Ch. [3] 38, 460).

Mesotartaric or **inactive tartaric acid** is obtained, together with racemic acid, when cinchonine dextro- or lævo- tartrate is heated for some time at 170° (Pasteur, C. R. 37, 162), or, according to Dessaignes (A. Suppl. 2, 242), by oxidation of sorbin by nitric acid.

It is best prepared by heating tartaric acid with one-seventh to one-tenth of its weight of water to 165° for two days in a closed vessel, crystallising out the racemic acid, converting the residue into the acid potassium salt, and removing the dextrotartrate by crystallisation. The more soluble mesotartrate remains in solution. The temperature should not be too high, as at 175° mesotartaric acid is almost entirely converted into racemic acid (Jungfleisch, Bl. [2] 19, 99).

Mesotartaric acid crystallises in readily soluble rectangular plates melting at 140° (Dessaignes, Bl. 1, 34), and containing one molecule of water, or in large anhydrous prisms resembling tartaric acid. A considerable number of mesotartrates are known. The calcium and potassium salts are more soluble than the dextrotartrates.

Meta-tartaric acid is obtained by fusing dextrotartaric acid as an amorphous deliquescent mass whose solution reproduces dextrotartaric acid on boiling. It yields salts of greater solubility than dextrotartrates, into which they are converted on boiling the solution (Erdmann, A. 21, 1; Laurent a. Gerhardt, A. 70, 348).

Dextrotartaric or **common tartaric acid** is obtained synthetically by boiling silver dibromosuccinate with water:

$$\left\{\begin{matrix}\mathrm{COAgO}\\ \mathrm{CHBr}\\ \mathrm{CHBr}\\ \mathrm{COAgO}\end{matrix}\right. + \mathrm{H_2O} = \left\{\begin{matrix}\mathrm{COHO}\\ \mathrm{CHHO}\\ \mathrm{CHHO}\\ \mathrm{COHO}\end{matrix}\right. + 2\mathrm{AgBr}$$

(*v.* Perkin a. Duppa, C. J. 13, 102; Kekulé, A. 117, 121).

It appears also to be produced, together with glycollic acid, when an alkaline solution of ethyl oxalate is reduced by sodium-amalgam (Debus, C. J. 25, 365).

Dextro-tartaric acid occurs in the free state, or, more often, as the acid potassium salt, and to a small extent as the calcium salt, in association with oxalic, malic, citric, and probably racemic acid, in tamarinds, mulberries, sorrel, cucumbers, and many other plants. It occurs in large quantity in the juice of the grape, which furnishes all that found in commerce.

When the grape juice ferments, the potassium bitartrate is gradually deposited, on account of its less solubility in the alcohol produced, partly as a crystalline crust on the sides of the vat and partly with the 'lees,' which consists of yeast and the various suspended matters of the must. The crust is known as 'argol,' and when recrystallised produces 'tartar,' which by further crystallisation is converted into 'cream of tartar,' technically known as 'cream.'

The quality of lees, argol, and tartar varies enormously. Superior argols are equal to tartar, while inferior varieties are little better than lees. The tartaric acid in argols varies from 40–70 p.c., and that in lees averages about 25 p.c., but varies within wide limits. Lees from 'plastered wines'—*i.e.* from those in which baked gypsum or 'yeso' has been trodden with the grapes, as in Spain, Cyprus, and the Greek Islands, the Marsala district of Sicily, and the South of France contain very little tartar, the acid being mostly present as the calcium salt.

The best class of coloured tartars consist of nearly pure bitartrate. That of Messina usually contains 76 p.c. of tartaric acid, 1½ to 3½ p.c. of which is present as the calcium salt, while that from St. Antimo contains 74–75 p.c., of which the calcium salt constitutes 3–4½ p.c. Vinaccia tartar, which is obtained from the skins and solid matters of grapes, contains about 70–73 p.c. of tartaric acid, 5–7 p.c. being calcium tartrate. Scheurer-Kestner (Rep. de Chim. Appliq. 1861, 39) has found as much as 45 p.c. of calcium tartrate in crude tartar.

Of the products imported into England, tartars come principally from Naples and Messina, argols from Messina, and lees from Messina and other parts of Sicily. The imports to London in 1890 were:—Italian tartar, 500 tons; argol and lees, 3,000 tons, of which the argol did not constitute above a tenth; cream of tartar, 1,000 tons, of which 150–200 tons came from Germany, 100 from Italy, 200–300 from Spain, and the remainder from France. About 1,200 tons of the acid were made in England in 1890, and about 1,200 tons were imported, chiefly from Germany. According to Thorn (Chem. Zeit. 35, 533), the following is the approximate annual production of different countries, in kilos:—Austria and Hungary, 500,000; Germany, 700,000; France, 300,000; Italy, 200,000; Spain, 50,000; United States, 1,200,000.

The following table shows the composition of tartars and lees from different localities (Warington, J. Soc. Arts, 1876, 370):—

—	Messina tartar	St. Antimo tartar	French lees (plastered)	Spanish lees (plastered)	Spanish lees (unplastered)
Tartaric acid as acid tartrate	74·05	69·34	4·48	5·27	22·66
Tartaric acid as neutral tartrates	2·60	4·66	21·34	19·13	11·67
Tartaric anhydride	67·408	65·120	22·721	21·472	30·210
Sand	0·140	0·425	4·600	4·900	4·730
Silica	0·055	0·130	2·130	1·960	
Ferric oxide	0·053	0·086	0·394	0·351	0·214
Alumina	0·021	0·092	0·844	0·832	0·578
Phosphoric anhydride	0·041	0·068	0·527	0·486	0·569
Lime	1·081	1·778	10·567	10·600	4·514
Magnesia	0·025	0·041	0·327	0·363	0·209
Potash	23·236	21·773	1·868	2·123	7·115
Soda	—	—	0·100	0·060	—
Sulphuric anhydride	—	—	4·566	5·729	—
Carbon dioxide	—	—	0·435	0·388	—
Chlorine	—	—	0·040	0·042	—
Combined water	5·688	6·396	5·904	5·552	4·159
Water at 100°, with vegetable and undetermined matter	2·252	4·091	—	—	—
Water at 100°	—	—	11·305	10·694	9·750
Vegetable matter	—	—	33·672	34·448	37·952
	100·000	100·000	100·000	100·000	100·000

The following table shows the general composition of lees (Warington, *l.c.*) :—

—	Tartaric acid as		Total tartaric acid
	Potassium bitartrate	Calcium tartrate	
Italian (33 samples) .	24·10	6·1	30·2
Greek (14 samples) .	19·90	11·8	31·7
French (9 samples) .	17·30	6·0	23·3
Do. (30 samples) .	5·30	20·5	25·8
Yellow Spanish (59 samples) . .	8·70	18·2	26·9
Red Spanish (17 samples) . .	8·80	17·4	26·2

Analyses of a large number of tartars from various localities have also been published by Scheurer-Kestner (Wurtz, Dict. de Chim. [3] 234), and Schicht (*l.c.* and Polyt. Centralb. 1871, 1051).

The lees often contains calcium carbonate; also Spanish earth (a native aluminium-magnesium silicate used in fining wine) when obtained from Spain; gypsum when the wine has been plastered therewith, and resin when obtained from the Greek Islands. The vegetable matter contains considerable quantities of nitrogen.

Scheele's process for preparing the acid consisted in merely neutralising the solution of the tartar with chalk, and decomposing the precipitated tartar with sulphuric acid. By this process, however, only half the acid was extracted, the rest remaining in solution as normal potassium tartrate:

$$2C_4H_5O_6K + CaCO_3 =$$
$$C_4H_4O_6K_2 + C_4H_4O_6Ca + H_2O + CO_2.$$

The first improvement on this process consisted in the replacement of the chalk by lime, which produced a larger yield, although a portion of the calcium tartrate was retained in solution by the caustic potash produced. Lowitz (Aikin's Dict. of Chemistry [1807] ii. 405) next suggested the precipitation of the residual tartrate from the solution after the treatment with chalk, by addition of calcium chloride, and his process has been largely used (Hofmann, Reports of the Juries on the Exhibition of 1862, 111), although now superseded by a process attributed to Desfosses, and consisting in the replacement of the calcium chloride by the precipitated calcium sulphate obtained by treatment of calcium tartrate with sulphuric acid.

The processes at present employed differ according as tartar or lees is the material made use of.

The process employed in England for treating tartar (*v.* Warington, J. Soc. Arts, 1876, 371) consists in gradually adding the tartar to boiling water in which whiting is suspended, until the whiting is consumed and the tartar neutralised. A quantity of moist calcium sulphate sufficient to decompose the normal tartrate remaining in solution is then added, and the whole is agitated while still boiling for about two hours, so that a dense crystalline precipitate of calcium tartrate, together with the insoluble parts of the tartar, is obtained, leaving a solution containing potassium sulphate, together with a little normal potassium tartrate, a small proportion of which invariably remains undecomposed. The mother-liquor is evaporated, and the potassium sulphate crystallised out and sold. About 24 to 26 parts of whiting are required for 100 parts of the tartar.

The calcium tartrate, having been washed on a vacuum filter, is mixed with water and decomposed by dilute sulphuric acid, a portion of the solution being tested at intervals to ascertain when sufficient acid has been added; the test employed is calcium chloride, which gives no precipitate with the calcium sulphate contained in the solution, but precipitates the free acid.

The gypsum resulting from the decomposition is washed on a vacuum filter, and the liquors are evaporated in steam-heated leaden pans, or in vacuum pans. After partial concentration, the liquor is run off from the gypsum which has deposited on the side of the pan, and is concentrated to the crystallising point, when it is run into a tub and continuously agitated by a mechanical stirrer to produce a granular 'salt.' This system of crystallisation separates the salt in about a fifth of the time required for crystallisation by standing.

It has been proposed to add barium oxalate to the liquor to remove the calcium sulphate remaining in solution, and thus prevent its deposition in the pan (*v.* Thorn, Chem. Zeit. 35, 533).

The mother-liquor from the 'salt' is concentrated, and a second and third crop of crystals are obtained by 'granulation' as above; the residual dark-coloured impure solution is known as 'old liquor.'

The granular salt is redissolved, heated with animal charcoal which has been freed from calcium phosphate by digestion with hydrochloric acid, the solution is filtered, concentrated, and crystallised in cylindrical leaden pans about two feet deep. Tartaric acid thus prepared always contains lead.

The crystallisation is assisted by addition of sulphuric acid, in which the acid is less soluble than in water, as further noted below.

The mother-liquors are diluted and precipitated with whiting, and thus produce a further quantity of calcium tartrate, which is worked up as above. It is found, however, that the iron, alumina, and phosphoric acid introduced in the tartar, charcoal, whiting, &c., gradually accumulate in the liquors, and greatly reduce their crystallising power, so that continuously more and more sulphuric acid must be added to induce crystallisation. The old liquor finally becomes thick and yields no tartaric acid, although a considerable quantity remains in solution, together with a large amount of decomposition products, principally due to the action of the sulphuric acid. Warington (C. J. 989, 1875) has observed oxalic acid in these liquors.

The loss of acid in the manufacture varies from about 8 p.c. in works which have not been working sufficiently long to be affected by this trouble to 12 p.c. or more in works which have been carried on for several years without removal of the old liquors.

A process patented by Goldenberg, in which the bitartrate is decomposed by slaked lime, is described by Friedberg (Ph. [3] 13, 999; *v.* also

Eng. Pat. 4,684, 1878; Jacobsen's Chemische Industrie, 1879, 86, 238).

The manufacture of tartaric acid from lees and low argols is usually carried out by Kestner's process, which consists in dissolving the lees &c. in hydrochloric acid, which at once separates it from much of the organic impurities and colouring matter. The solution is precipitated by whiting or lime, and the precipitate treated as above (*v.* Hofmann, Reports of the Juries on the Exhibition of 1862, 112; and Scheurer and Kestner, Wurtz, Dict. de Chim. [3] 236).

See further regarding the tartaric acid industry: Warington (C. J. 1875, 942; J. Soc. Arts, 1876, 369), Grosjean (C. J. 1879, 342; S. C. I. 1883, 338), Scheurer-Kestner (Wurtz, Dict. de Chim. iii. 236), Wurtz (C. C. 1871, 713), Thorn (Chem. Zeit. 35, 533), and Kaemmer (Chem. Zeit. 9, 939).

Tartaric acid crystallises in large anhydrous monoclinic prisms of sp.gr. $\frac{7^\circ}{4^\circ}$ 1·7594 (Perkin, C. J. 1887, 362). The crystals become luminous in the dark when rubbed. They melt at about 172° (Warington, C. J. 1875, 943) with production of meta-tartaric acid and of some di-tartaric or tartralic acid $C_8H_{10}O_{11}$, which is formed in large quantities at a slightly higher temperature or by prolonged heating. The further action of heat produces tartrelic acid $C_8H_8O_{10}$, and, finally, its isomer, tartaric anhydride. Ditartaric acid is an uncrystallisable, deliquescent mass, which readily combines with water, especially on boiling, to reproduce tartaric acid. Warington (C. J. 1875, 943) describes a peculiar plastic soluble calcium salt, which appears to be a salt of this acid. Tartrelic acid forms yellowish, deliquescent crystals, convertible into tartaric acid by boiling with water, or into tartaric acid by fusion with metatartaric acid. Tartaric anhydride is a white or yellowish powder, slowly converted by cold water into a jelly, which passes successively into tartrelic, tartralic, and tartaric acids (*v.* Fremy, A. Ch. [2] 68, 353; [3] 31, 329; Laurent and Gerhardt, C. R. 27, 318; A. 70, 348; Schiff, A. 125, 129; Warington, C. J. 1875, 943).

According to Warington (C. J. 1875, 988) and Grosjean (C. J. 1883, 334), metatartaric acid exists in the concentrated tartaric acid liquors which have been long heated in the factory. Grosjean found that in a solution of tartaric acid heated four hours in a water-bath, after a crust had formed on the surface, as much as one quarter of the acid had been altered. The production of metatartaric acid is reduced by the presence of much sulphuric acid. In dilute boiling solutions, and on prolonged standing even in the cold, metatartaric acid reverts to tartaric acid. A part of the losses in the factory are probably due to the formation of metatartaric acid. The formation of di-tartaric acid in factory liquors is doubtful.

The dry distillation of tartaric acid produces pyrotartaric acid $C_5H_8O_4$; pyroracemic acid $C_3H_4O_3$; pyrotritartaric acid $C_7H_8O_7$; formic, acetic, and lactic acids; and a small quantity of dipyrotartracetone $C_8H_{12}O_2$ (Bourgoin, Bl. 29, 309), together with aldehyde, acetone, and other decomposition products (*v.* also Pelouze, A. Ch. [2] 46, 297; Böttinger, B. 9, 670; Liebermann, B. 15, 428).

A solution of tartaric acid saturated at 15° contains 57·9 parts of the acid (Gerlach, Spec. Gew. der gebräuchlichsten Salzlösungen &c., Freiberg, 1859, 24; J. 1859, 44) or 57·75 parts (Maisch, J. 1865, 392). The sp.gr. tables published by these observers and by Schiff (A. 113, 189) agree closely. Gerlach's results are as follows:—

Sp.gr. at 15°	Per cent. of acid in solution	Sp.gr. at 15°	Per cent. of acid in solution
1·0045	1	1·1505	30
1·0090	2	1·1560	31
1·0136	3	1·1615	32
1·0179	4	1·1670	33
1·0224	5	1·1726	34
1·0273	6	1·1781	35
1·0322	7	1·1840	36
1·0371	8	1·1900	37
1·0420	9	1·1959	38
1·0469	10	1·2019	39
1·0517	11	1·2078	40
1·0565	12	1·2138	41
1·0613	13	1·2198	42
1·0661	14	1·2259	43
1·0709	15	1·2317	44
1·0761	16	1·2377	45
1·0813	17	1·2441	46
1·0865	18	1·2504	47
1·0917	19	1·2568	48
1·0969	20	1·2632	49
1·1020	21	1·2696	50
1·1070	22	1·2762	51
1·1124	23	1·2828	52
1·1175	24	1·2894	53
1·1227	25	1·2961	54
1·1282	26	1·3027	55
1·1338	27	1·3093	56
1·1393	28	1·3159	57
1·1449	29	1·3220	57·9[1]

[1] Saturated solution.

Of 90 p.c. alcohol 100 parts dissolve 29·146 parts of tartaric acid at 15°, while 100 parts of absolute alcohol at that temperature dissolve 20·385 parts (Bourgoin, Bl. [2] 29, 244; *v.* also Schiff, A. 113, 189). Of ether, 100 parts dissolves 0·393 parts at 15° (Bourgoin, *l.c.*).

Strong solutions of tartaric acid contract on dilution. Thus 500 c.c. of a solution of sp.gr. 1·338 require 505·508 volumes of water to produce 1,000 volumes (Warington, C. J. 1875, 942). The presence of much free sulphuric acid diminishes the solubility of tartaric acid at ordinary temperatures, and increases the difference between the solubility at high and low temperatures. A cold saturated solution of tartaric acid, when mixed with half its volume of concentrated sulphuric acid and cooled, gives an abundant precipitate of tartaric acid, while a hot solution of the acid in 1 volume of water and 1½ volumes of oil of vitriol (1·713 sp.gr.) deposits 70 p.c. of its acid on cooling. Thus a much larger proportion of tartaric acid is obtained in one crystallisation when sulphuric acid is present (Grosjean, C. J. 1883, 334).

Landolt (B. 6, 1075) gives the specific rotatory power of solutions of tartaric acid of varying strength. The power is much reduced by the presence of mineral acids, and is almost lost in solutions in methyl or ethyl alcohol or acetone, while solutions in dry acetone and ether, or dry acetone and chloroform, are feebly lævorotatory (Landolt, B. 13, 2329; *v.* also Pribram, M. 9, 485).

Tartaric acid is readily oxidised, usually with production of formic and carbonic acids. Hydriodic acid reduces it to malic, and finally to succinic, acid. Sulphuric acid carbonises it much more readily than citric acid. It precipitates gold and platinum from solutions, and reduces mercuric chloride to calomel.

It is used in certain photographic developing and printing processes. It is also employed medicinally (United States Dispensatory, 14th ed. 74), and for the preparation of baking powders, effervescing drinks, seidlitz powders, &c. It is used by the calico printer to liberate chlorine from bleaching powder; in the production of steam blues and greens, aniline black, &c.; as a 'resist' for aluminium and other mordants, and in the discharge colours for Turkey red. It is also used in the mordant bath in dyeing wool, and for brightening the colour of silk after dyeing.

Tartaric acid forms a large and important series of well-defined single and double salts.

Potassium tartrate $C_4H_4O_6K_2$ is obtained by neutralising the bitartrate with potassium carbonate. It forms monoclinic prisms, soluble in 66 parts of water at 14°C., and is used in medicine (*v.* United States Dispensatory, 14th ed. 1404; Brit. Pharm. 1885, 332). When mixed with an acid, the solution precipitates potassium bi-tartrate.

Potassium bi-tartrate, cream of tartar $C_4H_5O_6K$ constitutes the only source of tartaric acid and tartrates. It occurs in the juice of the grape, and is deposited on fermentation on account of its lesser solubility in alcohol, partly as a crystalline crust known as argol and partly with the 'lees.' The composition of these substances and statistics of their production have been given under the manufacture of the acid. The argol &c., when heated with water, yields slightly coloured crystals of the purer salt, which is known as 'tartar.' This may be dissolved in hot water, and cleared from colouring matter &c. by addition of clay or egg albumen, filtered, and crystallised with production of the commercial 'cream of tartar.'

According to Kaemmer (Chem. Zeit. 9, 939), tartar is obtained from the marc and lees in Italy as follows: the dried lees is ground in a mill, boiled in coppers holding about 1,200 litres with 10 to 12 parts of water, and the solution is left for five or six days, any crystals which form being prevented from falling to the bottom of the vessel. The crystals and the liquor are then removed, and the residue is boiled with sulphuric or hydrochloric acid, and the solution treated with potash to convert the tartaric acid into the acid potassium salt. The crystals obtained are mixed with the first crop and sold as crude tartar or recrystallised.

Potassium bi-tartrate crystallises in aggregations of small, hard rhombic prisms, permanent in air, and having a sp.gr. of 1·973 (Schiff, J. 12, 16). The solubility of the salt in 100 parts of water is as follows, according to Warington (C. J. 1875, 946); Chancel (J. Ph. [4] 1, 348); Alluard (C. R. 59, 500); and Kissel (Fr. 8, 410):—

—	Warington	Chancel	Alluard	Kissel
14°C.	0·431	—	—	—
15°	—	0·453	—	0·493
20°	—	0·553	0·57	—
22°	0·600	—	—	0·615
25°	—	0·670	—	—
80°	4·027	—	4·50	—

Kissel (*l.c.*), Chancel (*l.c.*), and Buchner (D. P. J. 228, 167) have determined its solubility in dilute alcohol at different temperatures. According to Chancel, 100 parts of alcohol of 10·5 p.c. dissolve the following amounts:—

0°C.	1·41	15°C.	2·53
5°	1·75	20°	3·05
10°	2·12	40°	7·00

It requires 2,000 parts of proof spirit for solution, and is practically insoluble in much stronger spirit.

The alteration of the solubility in water by the presence of other substances has been examined by Destouches (Bull. Pharm. 1809, 468) and Warington (C. J. 1875, 947), and the latter has determined the solubility in acid solutions of equal acidity, *i.e.* of such strength that equal volumes require equal quantities of alkali for neutralisation; and in potassium acetate and citrate:—

——	Grms. of acid or salt in 100 c.c.	Grms. of bitartrate dissolved in 100 c.c.
Water . . .	—	0·422
Acetic acid . .	0·8106	0·422
Tartaric acid .	1·0331	0·322
Citric acid . .	0·8448	0·546
Sulphuric acid .	0·6853	1·701
Hydrochloric acid	0·5037	1·949
Nitric acid . .	0·8445	1·969
Potassium acetate	1·3875	0·744
Potassium citrate .	1·3966	0·843

The solubility is thus diminished by the presence of tartaric acid, and increased by the presence of other acids. The solubility of potassium bi-tartrate in hydrochloric acid of various strengths has been determined by Warington (*l.c.*). The solubility of potassium bi-tartrate in water is greatly diminished if potassium chloride, sulphate, or nitrate be also present. Grosjean (C. J. 1879, 348) showed that, while the solubility in water at 12° was 1 in 262, the solubility in a 5 p.c. solution of potassium chloride was 1 in 3,213, and in a 10 p.c. solution 1 in 4,401.

When heated, potassium bitartrate yields a mixture of carbon and potassium carbonate used as a reducing agent under the name of 'black flux.' Potassium bitartrate is largely used in the preparation of effervescing drinks, baking powders &c., and in medicine; also in the mordant bath for wool-dyeing, in conjunction with alum, iron salts, stannous chloride &c., apparently producing double salts, which are more effective as mordants.

Cream of tartar dissolves readily in a solution of boric acid or borax (Le Fèvre, Mémoires de l'Acad. Royale, Paris, 1732), and the product is used medicinally under the name 'soluble cream of tartar.' It is best prepared by dissolving a mixture of 4 parts of cream of tartar and 1 of boric acid in 24 of water, and heating until most of the water is driven off (*v.* also Robiquet, J. Ph. 21, 197). The salt prepared with boric acid is a white powder, which is permanent in the air, whereas that prepared with borax, and known in the German Pharmacopœia as 'Boraxweinstein,' is deliquescent.

Sodium tartrate $C_4H_4O_6Na_2 2H_2O$, crystallising in rhombic prisms or needles, and *sodium bitartrate* $C_4H_5O_6NaH_2O$, crystallising also in the rhombic system, are both readily soluble.

Potassium sodium tartrate, Rochelle salt $C_4H_4O_6Na.K.4H_2O$ is prepared by neutralising a boiling solution of cream of tartar with sodium carbonate. On cooling the solution, the salt crystallises in large rhombic prisms of sp.gr. 1·767 (Schiff, J. 12, 16), soluble in about 15 parts of cold water, and much used in medicine as a mild aperient. It forms the active constituent of most seidlitz powders.

Solutions of Rochelle salt deposit potassium bitartrate on addition of hydrochloric, acetic, citric, nitric, or sulphuric acid (Thomas, C. J. 1878, 375).

The normal and acid tartrates of *ammonium*, *lithium*, *cæsium*, and *rubidium* are all readily soluble. They are of no technical importance.

Calcium tartrate $C_4H_4O_6Ca.4H_2O$ (dried over oil of vitriol) occurs in small quantity, together with the acid potassium salt, in many plants, and is invariably found in argol and lees, as described above. It crystallises in rhombic prisms or pyramids, but is frequently deposited from dilute solutions in aggregates of fine radiating needles, which gradually become converted into isolated pyramids or prisms.

It may be prepared by adding a calcium salt to a solution of a tartrate. It dissolves in 6,265 parts of water at 15°, and in 352 parts at 100°, and is also soluble in solution of ammonium salts and alkalis, and, when recently precipitated, in chloride and nitrate of ammonium (Brett, P. M. [3] 10, 96).

It also dissolves in mineral acids, and in acetic and tartaric acids, and, in a lesser degree, in potassium bitartrate and other soluble tartrates. It forms double salts with the alkaline tartrates.

According to Grosjean (S. C. I. 1883, 338), calcium tartrate is decomposed by digestion with a hot, strong solution of potassium or sodium sulphate, almost all the tartaric acid passing into solution as the potassium or sodium salt, while the calcium is converted into a double sulphate with the alkali. In the case of sodium sulphate the action is reversed on cooling, and a considerable quantity of the tartrate is again precipitated.

Calcium tartrate is not precipitated by addition of calcium sulphate solution to a solution of a neutral tartrate, but digestion with the moist sulphate almost entirely precipitates it. Warington (*l.c.*) describes a curious form of calcium tartrate which forms in cold dilute solutions on standing. After the usual crystals have formed, tufts of fine long needles commence to appear, accompanied by fine aggregates of needles forming stars &c., and floating in the liquid. They disappear in a few days, and leave only a small bulk of the ordinary salt.

The acid salt $(C_4H_5O_6)_2Ca$ is formed by dissolving the normal salt in tartaric acid, and is much more soluble than the normal salt.

The *strontium* and *barium* tartrates are more soluble than the calcium salts.

Magnesium tartrate $C_4H_4O_6Mg.4H_2O$ is obtained as a crystalline crust by evaporating a solution of magnesium carbonate in tartaric acid, and is soluble in 122 parts of water at 16°. The acid salt $(C_4H_5O_6)_2Mg$ is obtained as a crystalline salt soluble in 52 parts of water at 16°, when magnesium carbonate is dissolved in excess of tartaric acid. Double salts of magnesium, with potassium, sodium, and ammonium, are known.

A magnesium salt (magnesium ditartrate ?), prepared by neutralising with magnesium carbonate tartaric acid which has been fused and heated near the fusing point until no more bubbles are evolved, has been proposed as a substitute for magnesium citrate (Leger, Ph. 1873, 29). The solution of this salt, unlike that of the ordinary tartrate, remains without turbidity for some weeks.

Aluminium tartrate. The salt formed by dissolving alumina in tartaric acid forms a gummy non-deliquescent mass soluble in water, and capable of dissolving considerable quantities of alumina without becoming alkaline. A double salt of potassium and aluminium appears to be formed by dissolving alumina in cream of tartar. It forms an amorphous mass not precipitated by alkalis, and probably constitutes the active ingredient of the mixture of alum and cream of tartar used in the mordant bath for dyeing wool.

Silver tartrate *v.* art. SILVER SALTS &c.

Antimony tartrates *v.* art. ANTIMONY.

Lead tartrate $C_4H_4O_6Pb$ is obtained by addition of tartaric acid to a solution of a lead salt, as a white crystalline powder almost soluble in water, but readily dissolved by alkalis. An insoluble basic salt $C_4H_2Pb_2O_6$ is obtained by boiling an ammoniacal solution of the normal tartrate (Erdmann, A. 21, 19; Heintz, Z. für Chem. und Pharm. 1861, 17).

Copper tartrate is obtained as a greenish-blue crystalline powder of the composition $C_4H_4O_6Cu.3H_2O$, on addition of copper sulphate, to a normal tartrate. It dissolves in alkalis and ammonia, with formation of double tartrates, and the deep-blue solution is reduced, with precipitation of cuprous oxide, by heating with glucose and many other organic bodies (*v.* art. FEHLING'S SOLUTION).

Ferrous tartrate $C_4H_4O_6Fe$ is obtained as a white, almost insoluble, crystalline powder by boiling iron filings with tartaric acid.

Ferric tartrate $(C_4H_4O_6)_3Fe_2$ is obtained by dissolving the precipitated oxide in tartaric acid. The solution precipitates a basic salt on warming, but is not precipitated by addition of alkalis, on account of the production of a double salt. *Ferric ammonium tartrate*, which is employed in medicine, is prepared, according to the U.S. Dispensatory, 14th ed. p. 1214, by dissolving 6 oz. of tartaric acid in 2 pints of water, and neutralising it with ammonium carbonate, 6 oz. of tartaric acid being then added. Hydrated oxide precipitated from a solution of ferric chloride is then stirred in at 140°F. until no longer dissolved, and the solution is filtered, evaporated to a syrup at a temperature below 140°F., and dried on a glass plate, so that it may be obtained in scales.

It forms transparent garnet-red scales of sweetish taste, slowly but highly soluble in water to a neutral solution, but insoluble in alcohol and ether.

The *potassium salt* is similarly prepared and used. It forms ruby-red transparent scales soluble in about 4 parts of water, and sparingly soluble in alcohol. It decomposes at 150°C., with evolution of carbon dioxide and water.

Detection and estimation of tartaric acid. Tartaric acid and tartrates char readily when heated with strong sulphuric acid. To distinguish from citric acid or citrates, the substance is heated with pure concentrated sulphuric acid at 100° for forty minutes. In the presence of tartaric acid the liquid becomes blackened, even so little as 1 p.c. in the substance treated giving a brown shade, whereas citric acid only imparts a yellow colour.

Soluble tartrates give a white precipitate on addition of calcium chloride. The precipitated calcium tartrate may be tested by dissolving it in a minimum of acetic acid, adding a strong solution of potassium chloride, and shaking it, when a crystalline powder of potassium bitartrate is thrown down (Grosjean).

A delicate and characteristic test for tartaric acid consists in obtaining a silver mirror by warming an ammoniacal solution of silver tartrate. The solution to be tested is neutralised with soda or nitric acid and precipitated by addition of silver nitrate, and the washed precipitate is dissolved in a small quantity of dilute ammonia, and warmed in a test-tube at about 70° for a few minutes. Even a very small quantity of tartaric acid will produce a silver mirror on the tube.

Tartaric acid may be titrated similarly to mineral acids, phenolphthalein being the best indicator.

All tartrates leave a carbonate or oxide of the metal, together with carbon, on gentle ignition, and may be estimated by dissolving the residue in decinormal acid, and determining the amount of acid thus neutralised by standard alkali.

For the estimation of free tartaric acid, alone or in presence of citric acid, Allen (C. N. 31, 277) recommended the following process:—2 grms. of the sample are dissolved in 20 c.c. of proof spirit, and the filtered solution is diluted to 45 c.c. with proof spirit, treated with 5 c.c. of a cold saturated solution of potassium acetate, and stirred for ten minutes. The crystalline precipitate of potassium bitartrate is filtered off, washed with proof spirit, and, to remove any citrate carried down by the tartrate, is rinsed from the filter by a cold saturated solution of potassium bitartrate, and digested therewith for a few hours. It is then again filtered, washed with proof spirit, rinsed with hot water into a weighed dish, and weighed after driving off the water at 100°. The precipitate may be dissolved and titrated with decinormal alkali and phenolphthalein instead of being weighed.

For the estimation of the acid in tartrates and in factory liquors, argol, lees, &c., the processes of Warington and Grosjean must be employed. For complete accounts of these processes, and for methods of estimating the sulphuric acid, total organic acids, &c., *v.* Warington (C. J. 1875, 942) and Grosjean (C. J. 1879, 342; S. C. I. 1883, 338).

For the estimation in tartaric acid liquors which contain other organic acids, sulphuric acid, sulphates of potassium, calcium, iron, and aluminium, together with various other impurities, a quantity of the liquor containing 2 to 4 grms. of tartaric acid (about 30 to 40 c.c.) is treated drop by drop with constant stirring, with a saturated solution of potassium citrate until, the sulphuric acid having been converted into potassium sulphate, the citrate commences to act on the tartaric acid, with precipitation of potassium bitartrate, which appears in streaks on the sides of the vessel. A precipitation of potassium sulphate, which precedes the appearance of the bitartrate when much sulphuric acid is present, is easily distinguished from the bitartrate. A cubic centimetre of the citrate solution is then added for every grm. of tartaric acid supposed to be present. If a gelatinous precipitate appear, which never occurs when the liquor contains the usual amount of sulphuric acid, the estimation is repeated, with previous addition of citric acid. After continuous stirring for ten minutes at a temperature not exceeding 15°, the precipitate is filtered off and washed with a 5 p.c. solution of potassium chloride saturated with potassium bitartrate, and the precipitate and filter are transferred to a beaker, and titrated with decinormal alkali.

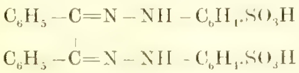
In presence of much sulphuric acid, potassium alum may be precipitated on addition of the citrate solution, in which case the results will be too low, on account of the solubility of potassium bitartrate in the washing liquid in presence of alum. To prevent this, phosphoric acid may be added before addition of the citrate, the liquid being filtered after ten minutes' stirring, before the appearance of a gelatinous precipitate of aluminium phosphate.

For the estimation of tartaric acid in tartar, Warington (*l.c.*) recommends the following process. The amount of potassium bitartrate in the sample is determined from the acidity. The neutralising power of the ash of the sample is then found. By subtracting from this the alkali belonging to the potassium bitartrate the amount of base existing as neutral tartrates is ascertained.

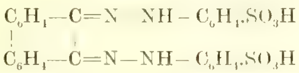
The method employed by Warington and Grosjean (C. J. 1879, 34) for the analysis of lees is as follows: A quantity of the finely-ground lees or argol, containing 2–2½ grms. of the acid, is heated on a water-bath with a little water until thoroughly softened, and a 25 p.c. solution of neutral potassium oxalate is then added in quantity sufficient to combine with the whole of the lime and leave an excess of about 1·5 grm. of oxalate. After heating, with frequent stirring, for fifteen minutes, the solution is almost neutralised with potash, and is further heated for a short time, and filtered through a small vacuum filter. The residue is washed six times, the washings being concentrated and added to the main filtrate; the total bulk should not exceed 50 c.c. To the solution is then added 5 grms. of potassium chloride, and citric acid in strong solution or crystals about twice the amount theoretically required to precipitate the whole of the tartaric acid as bitartrate. The solution is stirred for ten minutes, after which the precipitated potassium bitartrate is filtered off and washed with a 5 p.c. solution of potassium chloride, saturated with potassium bitartrate as above. The filter and precipitate are then placed in a beaker, and titrated with standard alkali and phenolphthalein.

Scheurer-Kestner (Chem. Zeit. 1883, 1601, 1260, 1362; 1885, 1356) determines tartaric acid as calcium tartrate. Five grms. of the crude tartar are dissolved in hydrochloric acid, filtered, the solution neutralised with sodium hydrate free from carbonate, and precipitated with excess of calcium chloride. After long standing, the calcium tartrate is collected, washed, and ignited. The neutralising power of the resulting carbonate is determined with standard acid and alkali, and the tartaric acid calculated therefrom.

TARTRAZINES. Dyestuffs of the tartrazine class have been obtained by substituting, on the one hand, phenylhydrazine sulphonic acid by its homologues and the naphthylhydrazine sulphonic acids, and, on the other hand, substituting dehydroxytartaric acid by such double ketones as benzil and phenanthraquinone. The dyestuffs, formed by benzil and phenanthraquinone by condensation with phenylhydrazine sulphonic acid, have the following constitutions:



$$\begin{array}{l} C_6H_5-C{=}N-NH-C_6H_4.SO_3H \\ \qquad\;\;| \\ C_6H_5-C{=}N-NH-C_6H_4.SO_3H \end{array}$$

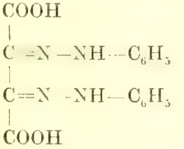


$$\begin{array}{l} C_6H_4-C{=}N-NH-C_6H_4.SO_3H \\ \;| \qquad\;\;| \\ C_6H_4-C{=}N-NH-C_6H_4.SO_3H \end{array}$$

In the phenanthraquinone compound two of the benzene rings are directly united in addition to being connected through the —C—C— group, which fact finds expression in the reddish-yellow colour of the dyestuff, the benzil dyestuff being a pure yellow.

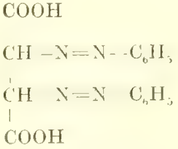
The tartrazines closely resemble the mixed azo- dyes, as the constitution of the two classes of bodies shows:

1



$$\begin{array}{l} COOH \\ | \\ C{=}N-NH-C_6H_5 \\ | \\ C{=}N-NH-C_6H_5 \\ | \\ COOH \end{array}$$

2



$$\begin{array}{l} COOH \\ | \\ CH-N{=}N-C_6H_5 \\ | \\ CH-N{=}N-C_6H_5 \\ | \\ COOH \end{array}$$

1 being the ordinary formula of the osazone of dihydroxy-tartaric acid or of unsulphonated tartrazine; 2, that of a mixed azo- dye. It is possible that the first formula represents an unstable compound, which at the moment of formation undergoes a molecular change, and becomes constituted as in the second type. This is supported by the fact, discovered by Zincke, that the hydrazone of *a*-naphthoquinone is identical with benzene-azo-*a*-naphthol. Again, Meyer finds that the hydrazone of mesoxalic acid prepared by E. Fischer is identical with benzene-azo-malonic acid obtained by saponifying the product of the action of diazobenzene chloride on the sodium compound of diethylmalonic ether. Japp and Klingemann also find the benzene-azo-propionic acid prepared by them identical with Fischer's hydrazone of pyruvic acid. Further, A. Bernthsen points out that the hydrazone of acridylaldehyde has all the properties of an azo- dye. Then, again, whilst Japp and Klingemann have proved that benzene-azo-acetone is a hydrazone compound, and not an azo- body, Claisen and Baeyer showed that certain similar compounds behaved, in certain reactions, more like azo- bodies. In the present state of knowledge, it is impossible to fix the constitution of these bodies, the mixed azo- dyes and the hydrazones, with certainty, for they appear to be substances so susceptible of molecular change as to react as azo- dyes in some cases and as hydrazones in others (R. Meyer, Mittheil. des K. K. Tech. Gew.-Museums, 1889, 49–55; S. C. I. 8, 536; *v.* Azo- colouring matters; also Hydrazone colouring matters).

TASMANITE *v.* Resins.

TAURINE. *Amidisethionic acid*

$$C_2H_4(NH_2)SO_3H.$$

A substance originally discovered by Leopold Gmelin in ox-bile, but found also in human bile, and, indeed, in all kinds of bile which contain taurocholic acid. Found also in the kidneys, lungs, muscles, &c. Is never found in the free state in healthy bile. Contained in many molluscs, in the blood of the shark, and in the liver, spleen, and kidneys of the ray. To obtain it from ox-bile, hydrochloric acid is added in slight excess, and, after filtering, the liquid is evaporated until a viscous resinous mass separates out; the watery liquid is decanted off and concentrated, when common salt, formed by the action of the hydrochloric acid on the sodium salts of the biliary acids, crystallises out. The solution is filtered and mixed with strong alcohol, when taurine separates out, which is purified by recrystallisation. Has been artificially obtained by heating ammonium chlorisethionate with excess of aqueous ammonia (Kolbe, A. 122, 33). Forms large transparent monoclinic prisms. Readily soluble in water (1 pt. in 15·5 pts. of water at 12°). Nearly insoluble in absolute alcohol. Is converted into *isethionic acid* when treated with nitrous acid (Gibbs, Am. J. [2] 25, 30).

TAUROCHOLIC ACID $C_{26}H_{45}NSO_7$. *Cholcic acid, sulpho-cholcic acid.* A monobasic acid existing mainly as a sodium salt in the bile. Crystallises in fine silky needles, readily soluble in water and alcohol. Yields taurine on boiling with acids.

TAXINE, TAXUS, *v.* Yew.

TCHA-LAN. A blue powder containing copper; used by the Chinese for obtaining a blue colour on porcelain (Ebelman and Salvétat, A. Ch. [3] 35, 338).

TEA. This term is usually understood to signify both the dried leaves of certain plants belonging to the natural order *Ternstrœmiaceæ* (notably two species of *Thea*—*T. chinensis* and *T. assamica*, or of hybrids between these two); and also the aqueous infusion prepared from them.

Tea has been used in China for centuries. In poems edited by Confucius, before 550 B.C., there are doubtful references to it. The writer Yo Lu—who lived during the Tang dynasty, which lasted from 618 to 906 A.D.—says that it was drunk in the sixth century, and that during the eighth century it became so common that a tax was levied on it. Arab writers speak of it in China in the ninth century, and it seems to have been introduced into Japan in 810, where its cultivation was commenced early in the thirteenth century. There was no knowledge of tea in Europe until after 1517, when intercourse began between Portugal and China. It was first brought to Europe in 1610 by Dutch merchants, and some years later was introduced into England. Pepys mentions having tasted it. The East India Company presented 2 lbs. of tea to Catherine, the Queen of Charles II., in 1664, and in 1669 they imported it directly from China. A Mr. Wickham, the agent of the East India Company in Japan, wrote to an officer-friend named Eaton, in 1615, asking for 'a pot of the best sort of chaw' (tea), and in Mr. Eaton's own accounts occurs the item, 'Three silver porringers to drink chaw in.' Garway, the first tea-dealer in London, issued in 1659 a broadsheet headed, 'An exact description of the growth, quality, and virtues of the leef of Tea.' In 1660 he bought a lot, and sold it according to quality at from 15*s.* to 50*s.* per lb. He had the infusion 'made according to the directions of the most knowing merchants and travellers into those Eastern countries.' In 1666 there were not more than 100 lbs. of tea brought to Europe, and its price was as high as 60*s.* per lb. By 1725 the price had fallen to from 13*s.* to 20*s.* for black tea, and to from 12*s.* to 30*s.* for green tea. In 1745 the amount brought to England alone was 730,000 lbs., and in 1800 the infusion had become a very general beverage in this country. The following table gives some idea of the growth of the consumption of tea in the British Isles during the last ninety years:—

—	Amount consumed (lbs.)	Amount per head of population (lbs.)
1800	23,723,000	—
1835	—	1·5
1840	32,000,000	—
1850	51,000,000	—
1853	58,000,000	2
1860	77,000,000	—
1870	118,000,000	—
1871	123,500,000	3·9
1876	186,000,000	—
1880	208,404,333	—
1890	194,009,000	—
1891[1]	202,457,000	5·33

[1] Furnished by Messrs. Thompson, Mincing Lane.

The reduction of duty has no doubt aided this rapid increase. From about 1833, when the monopoly of the East India Company was withdrawn, the high duty of 6*s.* or 8*s.* per lb. was gradually reduced until in 1865 it was 6*d.* per lb. Since then Mr. Goschen has reduced it to 4*d.*, and the price of tea has still further diminished. In China the price has, of course, been always much lower. In Canton some years ago the average price was said to be 8½*d.* per lb., so that the growers must have sold it at 5*d.* or 6*d.*

China and Japan were the only great tea-producing countries until this century, although the plant was known as far back as 1780 to be growing in India. In 1788 Sir Joseph Banks pointed out the advantages that would follow from the cultivation of tea in India, and in 1820 Mr. David Scott sent leaves to Calcutta from wild tea-plants growing in the districts that Sir J. Banks had named as suitable for planting. Unfortunately it was stated that the leaves sent belonged to the genus *Camellia*, and hence no action was taken in the matter.

Early in the fourth decade of this century Mr. C. A. Bruce noticed the tea-plant growing wild in the jungles of Assam, and in 1839 he received a gold medal from the Society of Arts for this discovery, and for successfully growing and preparing China tea in India.[1] Lord William Bentinck, when Governor-General, formed a committee to introduce the cultivation of tea into India; and in 1834 Dr. Wallish admitted that David Scott had been correct with regard to the leaf. The Government committee at first sent to China for seed and for skilled manufacturers, but Captain Jenkins again pointed out the indigenous *Thea assamica*, and this was used for some years.

In 1836, 1 lb. of tea was sent from India to London; in 1837, 5 lbs.; in 1838, 12 small boxes; in 1839, 95 boxes. In 1839 the Assam Tea Company was formed, which in 1840 bought one of the Government tea-gardens that had failed, and the cultivation has been carried on by private enterprise ever since. Government, however, was not satisfied with the amount of success attained, and a few years afterwards sent Mr. Robert Fortune to China to study the cultivation and manufacture of tea, and to bring seeds and plants thence to India. He found excellent tea grown and made in the Chusan Islands, and in the neighbourhood of Ning-po and of the Temple of Tein-tung, twenty miles inland; but as this was only for home consumption, he determined also to see and get seeds and plants from the districts of the interior, though this was forbidden to foreigners by Chinese law.

In 1849 he took his young tea plants to Hong Kong, and sent them in four different vessels to Calcutta. In April 1850, he returned to Shanghai and the north to get implements and engage manufacturers to accompany him. Altogether he introduced more than 12,000 plants into India, and went carefully over the chief tea districts there, travelling up the Ganges and beyond Allahabad. The plantations over the principal tea districts there lay about 29° and 30° N. lat. and 78° and 79°E. long. and were chiefly in the neighbourhood of Almorah, situated about 4,000 and 5,000 feet above the sea. The principal districts now are: Upper and Lower Assam, Dehra Doon, Kumaon, Darjeeling, Chittagong,

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[1] Mr. Bruce's right to this medal was disputed by Captain Charlton, who said he had pointed out the indigenous Assam tea-plant in 1832. The honour of its discovery has also been claimed for Moneram Dewan, a native.

Cachar, Arracan, Sunderbund, Chota Nagpore, and (in Madras) the Nilgiris. Kumaon, Darjeeling, and Chittagong were first planted in 1864, and Chota Nagpore in 1872.

Though in India the native plant or a hybrid is now used (*v. Cultivation*), Fortune's introduction of Chinese growers and manufacturers to teach methods to the natives must have greatly aided the Indian industry.

It seems generally to be considered by those who have studied the subject that Indian teas are good for blending on account of their high flavour, but that in every mixture a China tea should preponderate.

The rapid increase in the amount of Indian tea imported into England may be seen from the following statistics:

In 1857 we received 121,000 lbs.; 1872, 31,000,000 lbs.; 1880, 45,371,704 lbs.; year ending May 31, 1890, 101,052,000 lbs.

India now supplies us with more than we get from China. Year ending May 31, 1890: From India, 101,052,000 lbs.; China, 90,097,000 lbs.; Ceylon, 34,206,000 lbs.; Java, 3,107,000 lbs.[1]

Many attempts at the cultivation and manufacture have been made in Ceylon. In 1868 the coffee plants were diseased and the crop failed, and greater attention seems from that time to have been paid to the cultivation of tea. The industry has grown enormously, as may be seen from the accompanying tables:

Imports from Ceylon.

Year	No. of lbs.
1873	23
1874	492
1875	1,400
1876	757
1877	2,000
1878	20,000
1879	100,000
1880	150,000
1881	500,000
1882	750,000
1883	1,500,000
1884	2,250,000
1885	3,750,000
1886	7,000,000
1887	11,250,000
1888	20,500,000
1891	47,405,000

Ceylon tea combines some of the good qualities of Indian and of Chinese tea, and it does not require blending, but, like Indian tea, it does not keep well. In this respect Chinese tea is much the best. Tea-dealers know this, and store smaller quantities of Indian or Ceylon tea than of Chinese. In comparison with Indian tea, Chinese is also more uniform in quality. The Indian growers are apparently inclined to attend more to quantity than to quality. Our increased importation from India is partly owing to the heavy export duties levied on tea by the Chinese Government. As that government is, however, now fully alive to the fact that it is beginning to be outstripped in the tea trade by India, it may very possibly before long lower these duties, or remove them altogether.

Table of each 100 *lbs. imported.*

—	China contributed	India contributed	Ceylon contributed	Other countries contributed
1864	92·55	2·84	—	4·61
1865	93·00	2·50	—	4·50
1866	93·74	3·88	—	2·38
1867	91·81	6·07	—	2·12
1868	91·77	5·89	-	2·34
1869	90·85	8·07	—	1·08
1870	89·06	9·17	—	1·77
1871	88·25	8·91	—	1·84
1872	86·80	8·89	-	4·31
1873	83·81	11·28	—	4·91
1874	81·90	10·12	0·30	6·90
1875	86·31	12·87	0·08	0·74
1876	84·03	14·99	0·05	0·93
1877	82·65	16·50	—	0·85
1878	80·88	17·29	—	1·83
1879	76·94	20·76	0·07	2·23
1880	76·43	21·81	0·08	1·68
1881	77·33	21·66	0·08	0·93
1882	72·88	25·43	0·24	1·45
1883	70·27	26·66	0·90	2·17
1884	67·22	29·55	1·03	2·20
1885	65·84	30·35	2·00	1·81
1886	62·99	31·85	3·10	2·06
1887	54·00	38·15	5·89	1·96
1888	47·46	40·34	10·10	2·10
1889	39·88	42·93	14·70	2·49
1890	31·00	45·00	21·00	3·00

Roughly speaking, the number of people all over the world who now drink tea may be estimated at 500,000,000. The European nations who consume most are Great Britain, Holland, and Russia. Next to Great Britain, the United States import more than any other country, but reckoned by the amount drunk per head the Australians are the greatest tea-drinkers in the world. The following table gives the amount consumed per head in six countries:

Australia 9 lbs. per head per annum; China, rather more than 5 lbs.; England, about 5 lbs.; Cape of Good Hope, 5 lbs.; Holland, 0·91 lbs.; Russia, 0·43 lbs.

Europe is supplied chiefly by China and India, and North America by Japan.

The following tables, compiled by Messrs. Wilson, Gow, & Stanton, show the amount of the different teas used for home consumption for the last four seasons:

		1887-1888	1888-1889
Indian .	. lbs.	85,618,830	91,368,785
Ceylon .	.	12,578,124	23,830,564
China, &c.	.	86,654,785	70,420,450
Total lbs. .	.	184,851,739	185,619,800

		1889-1890	1890-1891
Indian .	. lbs.	98,715,902	100,485,971
Ceylon .	.	29,497,964	40,459,705
China, &c.	.	57,911,285	57,104,922
Total lbs. .	.	186,125,151	198,050,598

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[1] Furnished by Messrs. Thompson, Mincing Lane.

Tea. United Kingdom.

	Imports				Consumption	
Year	British East Indies	China (Hong Kong and Macao)	Other countries	Total	Lbs.	Lbs. per head
	lbs.	lbs.	lbs.			
1873	20,326,882	133,307,196	8,710,317	162,344,395	132,022,155	4·1
1874	18,440,494	131,669,998	11,492,918	161,603,410	137,422,563	4·2
1875	25,784,866	170,966,836	1,525,570	198,277,272	145,458,120	4·4
1876	28,126,854	155,897,192	1,674,144	185,698,190	149,131,779	4·4
1877	30,957,295	154,996,561	1,561,428	187,515,284	151,275,237	4·5
1878	35,563,503	166,190,545	3,707,235	205,461,283	157,691,762	4·6
1879	39,236,433	141,435,474	3,838,472	184,510,379	160,652,187	4·6
1880	45,530,728	158,195,142	3,245,700	206,971,570	158,570,334	4·5
1881	46,054,392	164,541,989	1,866,196	212,462,577	160,225,789	4·5
1882	53,927,998	154,081,777	3,070,587	211,080,362	165,079,881	4·6
1883	60,994,402	156,170,385	4,840,732	222,005,519	170,812,697	4·8
1884	66,084,947	144,410,328	4,716,839	215,212,114	175,097,983	4·6
1885	68,635,100	139,838,344	3,901,927	212,375,371	182,455,982	4·0
1886	80,987,351	145,111,596	4,796,345	230,895,292	178,894,151	4·9
1887	97,830,117	119,739,116	5,194,054	222,763,287	183,635,885	4·9
1888	113,004,692	105,424,271	5,189,515	223,618,478	185,556,214	4·9
1889	127,160,409	88,848,574	5,593,677	221,602,660	185,621,800	4·9

The methods of making the infusion vary in different countries. In China a pinch of tea is put into the cup, boiling water is poured on it, and the infusion is drunk at leisure, even after it is cold, and without milk or sugar. The water to make it is got from a running stream if possible, otherwise from a spring, *not* from a well, and is boiled slowly. The methods prevailing in Japan are described further on. In England the old fashion of letting the tea 'brew' and constantly adding hot water to the same leaves, is dying out; and the best tea-makers pour boiling water on to the leaves, which have been put into a heated pot, let it stand on them for about five minutes, and then pour off the infusion or take out the leaves. The reason for this method is, that practically all the theine and oil are by that time in solution, whilst not more than a third of the astringent tannin has been extracted. In Russia, lemon-juice is added to the infusion. In Germany, rum is sometimes added, as well as cinnamon or vanilla. In Spain, lemon-verbena leaves are added.

The 'brick tea' used in West and North-West Siberia is said to be itself eaten, after the infusion has been drunk, mixed with sugar, milk, and butter or some other kind of fat.

Botany. The tea-plant (*Camellia chinensis*) belongs to the order *Ternstrœmiaceæ*.

Leaves. Lanceolate, serrate, acute, and thick. They are alternate, and their stalks are short. Their upper surface is green and glabrous, and their under surface sometimes hairy on the nerves. The veins from the midrib go nearly to the edge, and then unite to form an intra-marginal vein. The leaves are dotted with pellucid oil glands.

Flowers. White or slightly yellow, axillary, regular and hermaphrodite. Bracts, two or three below the calyx. There are five round and convex sepals, and five obovate obtuse petals (more rarely, six or more). The stamens are indefinite, monadelphous, and adhere to the petals by their base. The styles are three in number, with simple stigmas. The ovary is superior and three-celled, each cell containing from four to five pendulous anatropous ovules.

Fruit. Woody, forming a three-celled loculicidal capsule, which remains green for a long time. Each cell contains one exalbuminous seed, the remaining ovules never ripening.

Cultivation. Our chief authority on the cultivation and manufacture of tea in China is Robert Fortune, who published his 'Journey to the Tea Countries of China' more than forty years ago, and gives in it many interesting particulars about the cultivation and manufacture of tea, and of his adventures in getting to the interior disguised as a mandarin.

He states that the parts of the world best suited by climate for the cultivation of the tea plant are China, Japan, India, Ceylon, South America, parts of Australia, the shores of the Mediterranean, the middle of France, and Ireland. Java might be added to his list. According to him, it is worth while to cultivate the plant on a large scale only where labour is cheap. In his time, the rate of wages in the tea-districts of China was 2*d.* or 3*d.* a day.

A warm climate is essential. In the best districts in China the ordinary range of the thermometer in the summer at 3 P.M. is between 80° and 90°F.; it sometimes reaches 100°, and it rarely falls below 32° in winter.

The best position for a tea-plantation, if other conditions are favourable, is a slope facing the south, because on sloping ground there is natural drainage, and the soil does not get too wet; it ought never to be as wet as in rice fields. If flat ground is used, the tea-gardens are often artificially raised, and are always carefully drained. The spring rains are most beneficial, provided the drainage be efficient. There must be a constant supply of water, either from natural sources or by irrigation. Hilly districts are suitable, because the vegetable matter washed down from above enriches the gentler slopes and the level ground below. The plant flourishes best in rich loam mixed with sand and gravel. Oak-bearing land is considered extremely good for tea plants.

Fortune tells of three main tea-growing districts in China. In the Chusan Islands and at Shan-hing-foo (near the coast, lat. 30° N.) excellent tea was grown and made, but only for home consumption. The principal district for growing leaves which were to be manufactured into green tea[1] lay between 29° and 30° N. lat. and between 117° and 119° E. long., about 200 miles inland up the Hwuy-Chow or Green River. The plantations were originally on the Sung-lo Hill, but afterwards on the plain below.

The Bohea Mountains, among which was the great black-tea district, are approximately between 27° and 29° N. lat. and between 115° and 117° E. long. The finest Pekoes and Souchongs came from the northern side of the hills, but were almost entirely consumed at home.

The so-called 'Bohea tea,' which is an inferior kind, was not made among these mountains, but in the neighbourhood of Canton.

The seed—which is in appearance like a hazel nut, having an outer and an inner shell inclosing a kernel, and ripens about a year after the flower has faded—is gathered in October, and kept in sand and earth, in which it germinates, till March, when it is sown in rows. Holes are dug and left for about two weeks, then filled with surface soil, and three seeds are put into each hole about six inches apart. The best plant remains in the hole, and the others are transplanted to vacancies. The plants are about four feet apart, and the same distance separates the rows. About 6 lbs. of seed are required for an acre, which yield 2,722 shrubs. Sometimes the seeds are sown more thickly in corners of the tea-farm or in nurseries, and the plants transplanted when a year old at the beginning of the rainy season.

The wild plant (originally, probably, the *Thea assamica* of the forests of Northern India) may grow to a height of from thirty to fifty feet, but the cultivated plants are pruned and kept to a height of from three to six feet, so that they become well-spread, bushy shrubs resembling somewhat the 'Portugal laurel' in appearance. The leaves are not picked until the plant is three years old. It does not yield its full quantity till its sixth or seventh year, and in China leaves are seldom gathered from a plant more than twelve years old. A good cultivator takes care that some portion of his farm shall be resown every year.

In India, only those plants are allowed to *flower* which are to be kept for producing seed, the leaves of which are not to be made use of. Fortune introduced Chinese seed into India; but it has been found that the indigenous plant, or a cross between it and the Chinese varieties, yields better tea in India. Only such seeds as are used in India are imported into Ceylon.

The raw leaves yield only about one quarter of their weight of manufactured tea. The plants give in their third year about 80 lbs. tea, and in their fifth year about 280 lbs. tea per acre; in their most productive year 320 lbs. per acre. It is said that in their richest year in India now the yield is from 300 lbs. to 800 lbs. per acre.[1]

In Fortune's time, however, in India the leaves were plucked before the plants were old enough, and this reduced their productiveness; so that plants of eight years old, which should each have yielded 2 or 3 lbs. a year, gave only 2 or 3 ozs.

Manufacture. The two great classes of tea are *green* and *black*, the differences between them depending solely on the mode of manufacture. Sub-divisions depend on the *age of the leaves*, *i.e.* the time of the year they are gathered, and the *way they are rolled.*

The names of the chief of these sub-divisions are as follows:

Green Varieties.

Hyson. Leaf-buds and first leaf; picked in April.

Young Hyson.

Skin Hyson (which is only the refuse of teas).

Gunpowder. According to Dujardin-Beaumetz, this is simply carefully selected hyson. According to Johnston and Church, it is from a special plantation, and flavoured with *Olea fragrans*, the sweet-scented olive.

Twankay.

Pearl or *Imperial.* Dujardin-Beaumetz describes this as a kind of hyson, but coarser than the true hyson, and of a silver-green colour. Johnston and Church say that the true Imperial, which is excellent, is rarely sent to Europe, and that what we call 'Imperial' is a tea from the Chusan Archipelago flavoured with the *Olea fragrans.*

Black Varieties.

Pekoe. Youngest leaf and leaf-buds; picked in April. This is sometimes flavoured by the addition of orange, rose, or jasmine flowers. When with the first-named, it is called *Orange Pekoe.*

Assam Pekoe is said to be inferior to the Chinese.

Congou or *Congo.*

Moning.

Souchong. According to Dujardin-Beaumetz, the strongest of the black teas.

Pouchong.

Bohea. The same authority describes this as a mixture of various leaves, stalks, and dust. Knapp says it is the coarse leaves picked in September and October.

Caper (plain-scented). The dust of various teas made into hard grains by means of gum or rice-water.

A list of *Indian teas* given by Edward Smith in his 'Foods' contains these:

Fine Pekoe.
Pekoe. Small leaf.
Pekoe Souchong. Large leaf.
Souchong. Larger leaf.
Congou. Coarse, dark, old leaf.

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[1] It must be borne in mind that the difference between green and black tea lies solely in the mode of manufacture. Nevertheless, Mr. Bannister says, in his 'Cantor Lectures' (1890), that the Chinese plant makes the best green tea, while hybrids are best for black.

[1] This agrees with Mr. Richard Bannister's criticism on the Indian planters that they are rather inclined to think more of quantity than quality.

Broken Pekoe. Siftings of other Pekoes.

Pekoe-Souchong Souchong. Siftings of Pekoe-Souchong and Souchong.

Fannings. Siftings of Congou.

Indian teas given in Blyth's 'Foods' are:

Mayone.
Mayone Gunpowder.
Oolong.
Mannuna Kaisow.
Scented Pekoes.
Indian Souchong.
Assam.
Java.

Mr. Richard Bannister (Deputy Principal of the Inland Revenue Laboratory[1]) gives rather a different account of the names.

Taking them in the order of the age of the leaves when picked, beginning with the youngest, they are as follows:

a. *Flowery Pekoe.* }
b. *Orange Pekoe.* } 'Poco' means the white down of the under leaves.
c. *Pekoe.* }
d. *First Souchong.* }
e. *Second Souchong.* } 'Souchong' means 'small plant.'
f. *Congou.* 'Congou' means 'labour,' and is meant to express that great care is required in the preparation of this tea.

a, *b*, *c* mixed make *Pekoe.*

a, *b*, *c*, *d*, *e* mixed make *Pekoe-Souchong.*

According to the older authorities, the leaves are plucked three times a year. In April (that is in China just before the spring rains[2]); at the end of May or beginning of June; and towards the end of June, or, according to some authorities, in July. Sometimes there is a fourth gathering in the late summer or early autumn, but leaves of such a size[3] and age as they are then make only the common and coarser kinds of tea. In South Australia there are always four, and sometimes in wet seasons a fifth gathering. Women are generally, if not always, employed in India, and sometimes in China, for the picking.

Mr. Bannister states that a plant is picked as its successive 'flushes' appear, a 'flush' being the throwing-out of new shoots and leaves; and that the number of flushes in a season—that is, in from seven to nine months—varies from eighteen to twenty-five, according to the soil. Up to a certain point the more a plant is picked the more new shoots it throws out. At the end of the season each shrub is 3½ or 4 feet high, and about 5 feet in diameter. It is then pruned down to a height of 2 feet and a diameter of 3 feet, and thus it remains till the spring.

In the manufacture of *green tea* the object is to keep the colour and prevent fermentation; it is necessary, therefore, to roast as soon as possible after picking, and finish the whole process quickly.

In the manufacture of *black tea*, on the contrary, the leaves are dried slowly before manipulation, and one of the processes is that of fermentation.

Processes of manufacture of green tea.

Chinese methods.[1]

Steaming. To get rid of the raw flavour, and preserve the colour, the leaves are spread out in bamboo trays and fitted into a bamboo box, the bottom of which is a boiler. Robert Fortune seems to have mistaken this process for drying, and to have thought the whole of the steam coming off was the natural moisture of the leaves. Here the leaves remain for an hour or two. They then are exposed on tiled floors, or in shallow bamboo trays out of doors in the shade, to prevent their turning yellow, and are meanwhile separated from stalks and dirt.

Roasting. Half a pound of leaves at a time is put into a *kno* or iron pan, 10 inches deep and 16 inches in diameter, which is set in a brick stove over a brisk wood fire. Here the leaves are kept four or five minutes, and stirred all the time rapidly with the hand. When taken out they are moist and flaccid, though much vapour has been given off.

Rolling. The object of this is to break the cells, whose contents come out and spread over the surface of the leaf, so that a fine aroma is produced. This is done on the rattan table, where the leaves are rolled by hand into balls, shaken out again, and rolled once more, passing from hand to hand till they reach the head workman, who sees whether they have the proper twist. If they are right they are shaken out on flat trays or sieves, and allowed to cool for a few minutes.

The second roasting is done over a slow charcoal fire for an hour or an hour and a half, at the end of which the green colour is fixed, dull at first, but gradually growing brighter. During the second roasting one man moves and occasionally rolls the leaves, while another fans.

Sifting. This is first done by means of sieves of different sizes; then the leaves are winnowed on large bamboo trays, and finally they pass through the winnowing machine. This gets rid of dirt and impurities, and separates the different kinds of tea, according to size and twist of leaf.

During the sifting the leaves undergo a *third roasting* or *re-firing.* It was about five minutes before the end of this last roasting that the manufacturer used to add the Prussian blue &c. for colouring. This was done for the foreign market only, as this highly coloured tea was prized in Europe until it was discovered to be faced. The whole manufacturing process takes about ten hours. Sometimes the sorting and re-firing take place at Canton before exportation instead of in the interior.

The principal centre of the tea trade in the green-tea district of China was, in Robert Fortune's time, Tun-che or Huy-chow-foo (lat. 30° N., long. about 119° E.) The merchants bought their tea from the priests and farmers who grew and manufactured it; they refined, sorted, and made it up into 'chops.'[2] From this place part of the tea was shipped to go down the river to Hang-chow-foo and thence to Shanghai; part was sent over the hills to the west, and then down the river towards Lake Po-yang, on its way to Canton.

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[1] 'Cantor Lectures,' 1890.

[2] In April and May the monsoon changes from north-east to south-west, and causes the rainy season. From June to August the weather is extremely hot, and there is very little rain, but the dews are heavy.

[3] A full-grown leaf measures from 5 to 9 inches in length.

[1] Knapp's 'Chemical Technology.'

[2] A 'chop,' according to Edward Smith in his 'Foods,' means the amount of tea yielded by one plantation in one year. In this case it seems to denote some special weight or measure.

Japanese methods.[1]

These are very much the same as in China. The chief points are as follows:

1. After steaming, the leaves are spread on tables or straw mats, and *fanned* to cool and get rid of some of the steam.
2. First rolling takes place *before* roasting.
3. There are three rolling processes as well as three roastings. The leaves are rolled very delicately and lightly at first, but as they become drier and less sticky they are rolled more and more strongly, till they take their final twist.
4. The furnaces are made of bamboo and mud, six or eight in a firing-room.
5. Charcoal is burnt every time, and a bundle of rice straw is burnt on the top of the charcoal, as its ash prevents the contact of the charcoal with the air, and secures uniformity of heat.

Over this are three iron bars, on which rests an iron gauze. Upon the gauze is placed a wooden frame with a paper or iron bottom, and starch paste is rubbed on the paper to give a smooth surface and prevent the formation of dust.

6. The temperature of the first two furnaces is from 75°C. to 85°C., sometimes even 94°C. The third roasting takes place at a lower temperature, from 65°C. to 75°C.
7. After the last roasting there is a final drying, the leaves remaining all night spread on paper on the furnaces, which have been reduced to a temperature of from 35° to 40°C. by the removal of all the glowing charcoal.
8. The sifting to get rid of *dust* takes place before the third roasting, but the final *sortimenting* is the next process. The sieves are hung by string and gently swung to and fro, while the tea is lightly pressed by the hand, and the open blades are separated from the rolled leaves and stalks. After almost all the dust and open leaves have been blown off, the latter are finally picked out by hand. *Final firing* now takes place at a moderate heat for about seven minutes. At the ports, the merchants have the tea again fired and sortimented before it is packed for exportation.

Indian methods.

Machinery is almost exclusively used in India for the manufacture of tea, as insuring 'more cleanliness and uniformity' than the method by hand. Each process appears to be gone through once without necessity for repetition.

There seems to be less difference between the Indian and the Chinese mode of manufacturing green tea than there is between the methods of the two countries in making black. According to Mr. Bannister, the Indian method of making green tea is as follows:

The leaves are picked twice a day. Those which are brought in at 1 P.M. are partly manufactured the same day; those which come in at night are spread six inches thick till next morning. The various processes are:

1. *Drying* (if necessary).
2. *Roasting.* This is done in pans over fires till the temperature is 160°F., and the leaves are meanwhile vigorously stirred for seven minutes.
3. *Rolling.* This is done four times in succession, the leaves being dried in the sun between each rolling.
4. *Second roasting.* The leaves are returned to the pans, and roasted at the same temperature as before.
5. *Beating.* Bags are filled with the leaves, which are then beaten heavily. They remain in the bags all night.
6. *Third roasting.* During the stirring this time the temperature gradually falls from 160°F. to 120°F.
7. *Sifting and sorting.* The sieves are round and made of brass wire or cane, with wooden sides 3½ inches high. Before sifting, any red leaves there may be are carefully picked out.

The method of manufacture in *Ceylon* is the same as that in India.

Processes of manufacture of black tea.

Chinese methods.

A little of the soft stalk is picked with the young leaves and leaf-buds for black tea.

Withering. The leaves are spread on large bamboo trays or mats, and exposed out-of-doors for some hours. If leaves are gathered during the wet season, this first drying takes place indoors on frames standing some feet above pans of hot charcoal. This process renders the leaves soft and pliable; the stalks bend without breaking, and do not crackle when compressed.

Tossing and fermentation. In a cool building, or in the shade out-of-doors, the leaves are then tossed and gently patted till they are soft and flaccid. They then lie in heaps, covered with a cloth, and are carefully watched till they get a slightly reddish tinge, and give out a fragrant smell.

First roasting and rolling. This roasting is for five minutes in shallow iron pans over wood fires. The rolling is on rattan tables, the same as for green tea. Sometimes the rolling takes place first, and sometimes the roasting.

Exposure out-of-doors. The leaves are now shaken out thinly on sieves, and put out-of-doors on bamboo frames for about three hours. In the black-tea districts they are seen in front of all the cottages; and workmen go from one to another turning and separating the leaves. The day should be fine and dry, but not too hot. When dry enough, they are removed to the factory.

Second roasting and rolling. This roasting is in the same shallow iron pan as before, and the rolling on the same table.

Drying and rolling. The leaves are spread to a depth of about one inch in sieves, and these are put into tubular baskets called poey-longs, which are slightly contracted in the middle, and are 2½ feet long and 1½ feet broad, somewhat like a dice-box in shape. There are cross-wires a little above the contraction of each basket on which the sieve stands. The poey-long, whose mouth is covered by a bamboo tray, stands upright over a low stove built on the ground, and containing a small quantity of charcoal, so that the tea-sieve is about 14 inches above the stove. These stoves are built round three sides of a long narrow room, and are 2 or 3 feet deep and $5\frac{1}{2}$ inches high. While the rolling goes on, the balls of leaves are left standing in heaps till all are done. The drying and rolling go on alternately, either two or three times, till the leaves are dry and crisp and have the right dark colour.

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[1] 'Researches on the Manufacture of Various Kinds of Tea,' by Y. Kozai. Bulletin No. 7 of the Imperial College of Agriculture and Dendrology, Japan.

Sifting. This is done by means of large circular bamboo trays, and the large leaves, if necessary, are picked out by hand.

Final drying. The fires are covered to reduce the heat. The leaves are placed much more thickly in the baskets, and the workman makes a hole with his hand through the centre of those in each sieve, to equalise the heat and allow the charcoal vapours to escape. Here the leaves remain over a slow fire for two hours or longer. The mouth of the basket is quite closed by a tray. For home consumption in China tea is not dried quite so much, and it is kept for a year before use.

With regard to the 'brick tea,' manufactured in China for consumption chiefly in West and North-West Siberia, it may be stated there are three kinds. The blocks of the first kind are made in wooden moulds, and are pressed and dried by the hand; they are each 12 inches long and 7 inches wide, and weigh about $3\frac{1}{2}$ lbs. Thirty-six of these bricks cost about twenty-eight shillings. The second kind is better. Each cake measures $8\frac{1}{4}$ inches by $5\frac{1}{4}$ inches, and weighs $1\frac{1}{2}$ lbs., and a basket of eighty or ninety of these costs about thirty-four shillings. The third kind is made of black tea-dust, pressed by machinery into 'bricks' $8\frac{1}{2}$ inches long and 6 inches wide, each weighing about $2\frac{1}{4}$ lbs. A basket of sixty-four cakes costs thirty-three shillings.

The chief towns in the black-tea district of China are, according to Fortune, Tsong-gan-kien and Tsin-tsun. The merchants of these places bought tea from the cultivators, and packed it for the foreign markets, making up chops of from 300 to 600 chests each. The tea was carried part of the way on the backs of coolies, and part of the way in boats down the river to Ho-kow, a town of from 300,000 to 400,000 inhabitants, and the great emporium of the black-tea trade. Fortune describes the streams of coolies that he met on the road, and how careful they were not to place the chests on the ground even for a moment, lest the damp should damage the best kinds of tea. From Ho-kow the tea was sent on either towards Lake Poyang and down to Canton, or northwards to Shanghai.

Japanese methods.[1]

1. The out-door *withering* process lasts only about an hour. In wet weather it is done on a rough cloth in hot pans, or on bamboo sticks over a gentle furnace.

2. The next process after withering is *the first rolling.* Great care is taken not to lose too much sap: if not done between the hands, the leaves are rolled in a flat box, whose lid and bottom have rough steps cut in them, over which a piece of rough cloth is nailed. The purpose of rolling, however, is to get the sap out of the cells and on to the leaf, so that the infusion may have all the substances possible in solution.

Fermentation. The leaves are either formed into small balls, or spread and pressed together on trays. They are then covered over with a cloth, and exposed to the sun. This lasts from forty to sixty minutes, at a temperature of about 40°C. Too short a time does not get rid of the raw flavour: too long a time produces a sour flavour. The exact time depends on the character of the leaves and the temperature. The higher the temperature and the more succulent the leaves, the more quickly does fermentation take place. The right moment to stop is known by the colour of the inside of the ball or layer, the process being checked long before complete fermentation has taken place.

Exposure out-of-doors, called 'sunning.' Fermentation really continues slowly during this process, which lasts about an hour in bright weather, but longer when it is cloudy. In wet weather it is done indoors over a gentle furnace.

Second rolling, and drying or 'firing.' The drying is in poey-longs, as in China. A paper is spread at the bottom of the sieve to prevent leaves falling into the furnace and causing smoke, which gives a 'smoky-burnt' flavour to the tea. The temperature is at first about 65°C., or less, but is gradually raised to 75° or 80°C. The leaves are *not touched*, but the baskets are constantly removed, and the leaves re-spread in fresh baskets. The firing is finished when the leaves are brittle enough to break by a slight pressure between the fingers; and the red leaves are then removed by hand.

Sifting is done most carefully with sieves having meshes of exact sizes, each sieve used having smaller meshes than the last. The meshes vary from 3 inches square to 1·5 inches; and the smaller the leaves the better the tea.

It will be seen that the manufacture differs from that of China in the order of the processes, and the time of their duration, but is the same in principle.

All teas in Japan are re-fired in the 'godowns' of the exporters. This is to drive off any excessive moisture,[1] tea being extremely hygroscopic, and to destroy any germs which might, especially in the presence of moisture, cause the tea to decay on its voyage to other parts of the world.

It has been proved by experiments with leaves of other plants in Japan that steaming not only preserves their colour but prevents fermentation. This may be because the heat of the steam kills the organisms which produce fermentation. Hence, for black tea, the leaves must on no account be steamed, but withered, and then allowed to ferment. For green tea the leaves are steamed to prevent fermentation and preserve colour, and are manufactured quickly.

[1] Y. Kozai, *l.c.*

[1] Kozai gives the weight of moisture of ordinary tea in Japan as 10 to 11 p.c., and says that the re-firing before exportation reduces this to 3 or 4 p.c.

In Japan two other kinds of tea are manufactured, called respectively *kamairii* or *pan-roasted tea* and *tencha* or *flat tea*. The former is made simply by alternate roasting in an iron or bronze pan, and rolling on a table seven or eight times over. Till 250 years ago all tea was made so, but now it is rare. According to Y. Kozai this is sometimes made in China, and is known there as '*sencha*.' For *flat tea* the leaves are supplied from a special plantation. They are not rolled or touched by the hand at all, but are spread on stiff paper for firing by means of bamboo sticks, and are alternately collected and spread out till nearly dry. Then they are taken from the furnace, all the broken or yellow leaves removed, and fired again. The final drying lasts all night at a gentle heat, and the leaves are then separated into three classes. For use they are *powdered*, and drunk with the infusion.

Indian methods.

The processes are as follows:

1. *Withering* on fine basket-work trays in the sun.

2. *Rolling*. This is done either by the rolling machine or by a line of men on each side of a table, who pass the leaves from one end to the other. When soft and 'mashy,' and giving out juice, the leaves are made into a ball, the juice that has come out being mopped up constantly during the process.

3. *Fermentation*. The balls stand until fermented, and are most carefully watched, as the flavour and quality of the tea depend largely on stopping this process at the right moment, and only skilled tea-makers can judge of this. At the proper time the balls are broken up, and the leaves spread thinly on mats in the sun. When they get rather black they are collected and re-spread, so that all the leaves may be alike, but this does not take long, for

4. *Drying or Firing* should take place as quickly as possible after the fermenting process, to drive off all the moisture. This is generally done in McMeekin's chest of firing drawers, which consists of a set of trays one above the other, the bottom of each, on which the leaves are spread, being made of fine wire gauze, so that all the trays can be heated at once. Formerly charcoal fires always produced the heat, but now hot air is often used instead. When the tea comes out of this machine it is almost black, and has a very delicate aroma.

5. *Sorting*. In sieves to separate the leaves into the different kinds for commerce.

The selection of teas for the market requires great delicacy of taste, and is the special business of men known as tea-tasters. Dujardin-Beaumetz says that they taste a five minutes infusion made by adding 105 grms. of water to from 2 to 6 grms. of tea. Mr. Bannister gives the following as the method:—43½ grains tea are infused in 3½ ounces water poured on at 100°C., when 20 p.c. of the total extract is obtained, and 50 p.c. of the theine. The tasters then judge by the bouquet, flavour, and pungency of the infusion, which depend a good deal on the amount and the quality of the volatile oil. But tea-tasters do not judge only by the taste; they consider also the colour, uniformity, and age of the leaf. In old times the East India Company employed tea-tasters at Canton, but Chinese tea is now generally tasted in London.

Chemistry of tea. The analyses of air-dried tea differ according to whether the tea be green or black, where it has been grown, and other circumstances.

The most important constituents of tea are theine, tannin, ash, and essential oil. Of these it is generally found that there is rather more theine in black tea than in green, and a good deal more tannin in green (though, according to Alfred Hill, this rule is not without exceptions); the amount of ash is fairly constant; the quantity of essential oil is very small in both, but it seems to be larger in green tea than in black. The total matter soluble in hot water is larger in green tea than in black.

The paper on the manufacture and chemistry of various teas by Y. Kozai, of Japan, which has been already quoted, gives analyses of the tea-leaves (all of the same kind) from a certain plantation under three different conditions:—

1. Dried at 85°C.
2. Made into green tea.
3. Made into black tea.

The following are the results:—

—	Original leaves dried	Same made into green tea	Same made into black tea
Crude protein	37·33	37·43	38·90
Crude fibre	10·44	10·06	10·07
Ethereal extract	6·49	5·52	5·82
Other nitrogen-free extract	27·86	31·43	35·39
Ash	4·97	4·92	4·93
Theine	3·304	3·200	3·300
Tannin (calculated as gallo-tannic acid). .	12·91	10·64	4·89
Soluble in hot water	50·97	53·74	47·23
Total nitrogen	5·973	5·989	6·224
Albuminoid nitrogen	4·107	3·937	4·106
Theine nitrogen	0·956	0·926	0·955
Amido-nitrogen	0·910	1·126	1·163

100 parts of dried leaves yielded:—

Green tea	98·64
Black tea	95·47

From the above figures it follows that in the process of manufacture the change in the amounts of the various constituents was such as is shown in the following table, where (+) denotes the gain, (−) the loss in 100 parts of each constituent:

—	Green tea	Black tea
Dry matter	− 1·36	− 4·56
Crude protein	− 1·70	− 0·61
Crude fibre	− 4·98	− 7·94
Ethereal extract	−16·18	−14·33
Other nitrogen-free extract	+ 11·31	+ 21·21
Ash	− 2·42	− 3·01
Theine	− 4·49	− 4·92
Tannin	−18·67	−63·82
Soluble in hot water	+ 5·96	−11·69
Total nitrogen	− 1·08	− 0·61
Albuminoid nitrogen	− 5·57	− 4·58
Theine nitrogen	− 4·49	− 4·92
Amido-nitrogen	+ 22·75	+ 22·42

The loss in ethereal extract is considerable, because part of the tannin changes during manufacture to a form insoluble in ether. In black tea, however, which undergoes fermentation, acids are formed during the fermentation that are soluble in ether.

The slight loss of ash and of theine arises from the mechanical loss of sap during manufacture.

The loss of tannin occurs during the heating processes in the manufacture of both kinds of tea. In black tea there is loss also during fermentation, when the tannin decomposes into substances *insoluble* in hot water. This accounts for the fact that hot water extracts less from black than from green tea.

Altogether, the change from the original leaves is greater in black tea, because of the process of fermentation.

Though the physiological value of any variety of tea depends on the amount of its theine, Eder says (D. P. J. 229, 81, 1878; 231, 445, 1879) that this does not affect its *commercial* value, which depends on—first, amount of extractive matter in hot water; second, tannin; third, total ash; fourth, ash *in*soluble in water. Hence in his analyses he does not determine the theine. The following are his results:—

—	Tannin	Extractive matter in hot water	Total ash	Ash soluble in hot water
Black tea (average of 25 analyses)	10·09	38·7	5·62	2·75
Yellow and green tea (average of 9 analyses)	12·4	41·3	5·73	2·79

The following are general analyses showing the differences between green and black tea:—

GENERAL ANALYSES.

—	Congou at 2/10 (black)	Young Hyson at 3/0 (green)
Moisture	8 20	5·96
Theine	3·24	2·33
Albumin insoluble	17·20	16·83
Albumin soluble	0·70	0·80
Extractive by alcohol containing nitrogenous matter	6·79	7·05
[1]Dextrin or gum	—	0·50
[1]Pectin and pectic acid	2·60	3·22
Tannin	16·40	27·14
Chlorophyll and resin	4·60	4·20
Cellulose	34·00	25·90
Ash	6·27	6·07
—	100·00	100·00

Average of six varieties of China green tea. J. F. Geissler, in 'Nahrungs und Genuss-Mittel,' by J. König.

—	Maximum	Minimum	Average
Moisture	7·78	5·39	6·43
Half-hour extract	44·70	30·20	36·74
Total extract	50·00	43·30	46·56
Insoluble leaf	49·61	44·60	47·05
Tannin	19·11	11·87	14·57
Theine	2·86	1·52	2·02
Soluble ash	5·02	2·02	3·28
Insoluble ash	6·38	2·11	3·61
Ash insoluble in HCl	0·66	0·21	0·49

Average of eleven Congou black teas. J. F. Geissler ('Analyst,' 1884).

——	Maximum	Minimum	Average
Moisture	9·15	7·65	8·37
Half-hour extract	32·14	23·48	28·40
Total extract	37·06	27·48	34·35
Insoluble leaf	63·85	54·50	57·20
Tannin	13·89	8·44	11·54
Theine	2·87	1·70	2·37
Soluble ash	3·52	2·28	3·06
Insoluble ash	3·86	1·90	2·68
Ash insoluble in HCl	1·31	0·32	0·425

The general differences between Indian and China teas are:—

Indian contain a larger amount of extractive matter than China teas, more tannin, and more essential oil. It is the larger amount of oil that gives their high flavour to Indian and Ceylon teas.

Average of six Indian teas. J. F. Geissler ('Analyst,' 1884).

——	Maximum	Minimum	Average
Moisture	6·19	5·56	5·81
Half-hour extract	39·66	37·80	38·77
Total extract	45·64	41·32	42·94
Insoluble leaf	53·07	48·53	51·24
Tannin	18·86	13·04	14·87
Theine	3·30	1·80	2·70
Soluble ash	3·68	3·24	3·52
Insoluble ash	2·22	1·93	2·12
Ash insoluble in HCl	0·296	0·137	0·178

Indian black tea. W. M. Green (C. N. 1884).

Assam Pekoe-Souchong (leaves of medium age).

Extractive matter by hot water	43·54
Theine	1·50
Tannin	21·46
Nitrogen	3·37
Total ash	5·59
Soluble ash	4·31
Insoluble	1·28

The following circumstances affect the chemical composition of tea:—

1. *Age of leaves.* From Spring to Autumn, the percentage of water, crude protein, and nitrogen free extract continually decreases; the theine diminishes gradually; the crude fibre increases proportionally as crude protein decreases. The percentage of ethereal extract increases proportionally as nitrogen free extract decreases. The percentage of tannin increases slightly; that of substances soluble in hot water gradually diminishes at first, then increases slowly. The percentage of *total ash* slightly fluctuates, but the constituents change much.

Potash and phosphoric acid diminish, whilst the lime, magnesia, iron, soda, manganese, and sulphuric acid increase.

Silica and chlorine remain nearly constant.

Some of the above general statements are shown more exactly by the following figures:

	May p.c.	November p.c.
Water .	76	60
Theine .	2·85	0·84
Total nitrogen	4·91	2·67
Amido-nitrogen	0·66	0·08 (September) 0·01 (following May)

Probably a portion of the amido-nitrogen became theine nitrogen.

	May p.c.	November p.c.
Tannin . .	8	11 or 12
Ash . .	4·69	5·14

These results were obtained by O. Kellner in conjunction with K. Oku and K. Ogasawara, of Japan ('Landwirthschaftliche Versuchs-Stationen,' 1886, p. 370).

2. *Effect of light.* On a plantation of uniform conditions and similar plants, Y. Kozai tried what difference of chemical composition there would be between the leaves of plants grown under the usual conditions and those of plants screened from the light by wooden frames during the last three weeks of their growth before picking. He obtained the following results:

	Screened leaves	Leaves exposed to light
Theine . .	4·532 p.c.	3·784 p.c.
Total nitrogen .	7·835	6·945
Theine nitrogen	1·311	1·0943
Tannin	no difference.	

The screened leaves were bleached, and had a fine and peculiar aroma.

Kozai states that there is not actually more theine in the screened than in the exposed leaves; but that in the latter there is a preponderance of woody fibre which makes the total dry matter larger.

3. *Age of plants.* It has often been said that old plants make the best tea. This has not yet been thoroughly proved or disproved by experiment, but some researches by O. Kellner with M. Tanaka and B. Minari on plants aged 4, 7, 16, and 20 years respectively, show that

the amount of water decreases regularly with the age of the plant, and that all other changes are extremely irregular. The older the plant, the more manuring and pruning is necessary to get a good crop of leaves.

4. As to *manuring*, it appears that it has no effect on the chemical composition of the leaves, although it increases their number on each plant. Bannister, however, says: ‘A judicious system of manuring nearly doubles the yield of tea, *improves its flavour*, and *increases its strength*.’ Bush prunings, weeds, and general rubbish make a very good manure. Animal manure must be used with great care.

Theine may be considered the active principle of tea, physiologically speaking, since a large number, if not nearly all, of the various plants whose leaves are used for infusions, and take the place of tea, contain it. Wigner, contrary to Eder, asserts that the *commercial* value of tea also depends on the amount of theine it contains. The composition of theine is $C_8H_5N_2O_2$. It crystallises in needles, is colourless, odourless, and has a slightly bitter taste. It neutralises acids, combining with them to form salts. Crystallised from aqueous solutions, it forms a hydrate containing two molecules of water. It dissolves in 98 times its own weight of cold water. It volatilises at 385°C., therefore the idea that it is driven off during the drying of the leaves is erroneous, though a small amount of it is lost by the unavoidable mechanical loss of sap which adheres to the hands of the manufacturers and to the apparatus.

The published determinations of theine in tea vary greatly, but this is partly owing to the different methods used.

We give here only the more recent estimations made by methods of repute.

Bannister gives the following table of theine determinations made in the Inland Revenue Laboratory:—

Kind of tea	Price per lb.	Percentage of Theine
	s. *d.*	
Bohea . . .	1 7	3·31
Congou . . .	2 6	2·93
Young hyson. .	3 2	4·29
Gunpowder low .	2 6	3·18
,, good .	5 0	4·98
Assam, low . .	2 8	3·03
,, good . .	4 6	4·83

Determination of Theine in Ceylon and Indian Teas (Paul).[1]

—	Elevation at which grown	Moisture per cent.	Theine per cent.	
			Original tea	Dry tea
Ceylon teas.	Feet			
Penrhos	2,500	6·8	4·56	4·89
F. L. C.	—	6·0	4·56	4·85
Nahalma	300	5·6	4·54	4·80
Hairs from leaves	—	6·6	2·40	2·57
Hardenhuish Pekoe	3,500	3·8	4·08	4·24
Woodstock Pekoe Souchong . .	4,200	3·6	3·44	3·57
Radilla Broken Pekoe	4,800	4·6	4·10	4·30
Morton Pekoe	400	4·2	3·98	4·15
Penrhos Broken Pekoe	2,500	6·4	4·64	4·96
Strathellie Orange Pekoe	2,000	5·4	4·10	4·33
Nahalma Orange Pekoe	300	5·4	4·06	4·29
Venture Orange Pekoe	4,300	5·4	3·74	3·95
St. Leys Pekoe Dust	4,600	5·6	3·46	3·66
Venture Pekoe Souchong	4,300	4·8	3·40	3·57
Venture Broken Orange Pekoe . .	4,300	6·6	3·98	4·26
Calsay Pekoe Souchong	5,000	6·2	3·22	3·43
Venture Pekoe	4,300	5·6	3·48	3·68
St. Clair Orange Pekoe	4,200	4·6	3·90	4·09
Indian teas.				
Pekoe Tips, picked out	—	7·56	4·27	4·62
Broken Pekoe	—	7·00	4·48	4·81
Pekoe	—	6·40	4·16	4·44
Orange Pekoe	—	4·80	4·66	4·89
Pekoe	—	5·60	4·48	4·74
Broken Pekoe	—	4·80	3·76	3·95
Pekoe	—	5·40	3·66	3·86
‘Weak’ Tea	—	6·80	4·06	4·35
‘Strong’ Tea	—	5·80	4·18	4·43
Mixture	—	6·00	3·64	3·87

Estimation of theine in tea. Hilger recommends the following plan:—10 to 20 grms. of the sample of tea are submitted to three successive treatments with boiling water. A slight excess of basic lead acetate is added to the filtered extract, the precipitate being collected, washed and decomposed with hydrogen sulphide. The filtered solution from which the lead has thus been removed is evaporated to dryness with addition of pure sand, granular marble, magnesia or chalk. The dried mass is now thoroughly extracted with chloroform in a Soxhlet's apparatus, the residue left after evaporation of the chloroform being dried for three hours at 100° and weighed. By repeatedly crystallising the residue from water or alcohol it may be obtained colourless.

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[1] Given in R. Bannister's ‘Cantor Lectures’ for 1890.

Waage has examined 37 methods proposed or used for the determination of theine, and gives preference to the methods of Mulder, Fricke, Stahlschmidt, and the one described above, but considers Mulder's method with some slight modifications the best. The modified method is as follows:—10 grms. of tea are extracted by four treatments with boiling water, taking altogether four hours' time. The filtered extract, measuring about 2 litres, is evaporated to a syrup, mixed with 2 grms. of pure calcined magnesia and 5 grms. of sand, and, after being thoroughly dried, is submitted to extraction with anhydrous chloroform in a Soxhlet's apparatus. The chloroform is evaporated, a slightly coloured residue being left, which contains fatty and resinous matters. These impurities are removed by dissolving the residue in hot water and filtering; the filtrate is evaporated to dryness and weighed, after being heated to 100° for two hours.

M. Hoffmann and R. Tittelbach also recommend Mulder's method, but the former considers it necessary to treat the aqueous extract with lead acetate to remove tannin and colouring matters as much as possible, precipitating the lead from the filtrate with hydrogen sulphide (An. Ph. 223, 828; S. C. I. 8, 822).

Tannin. Wynter Blyth states that if any tea gives less than 6 p.c. of tannin its genuineness may be suspected. Wigner's analyses give the following results:

	Tannin p.c.
Mayon Young Hyson tea . .	39·0
Very choice Assam . . .	33·0
India Young Hyson . . .	39·0
Assam (from Dr. McNamara's garden)	27·7
Caper, mixed	42·3

The amount of *ash* is nearly the same in all teas, from 5 p.c. to 6 p.c. According to Blyth, it is always rich in alkaline salts. Zöller found its constituents are as follows:

Potash	39·22 p.c.
Soda	0·65
Magnesia	6·47
Lime	4·24
Oxide of iron	4·38
Manganous oxide . . .	1·03
Phosphoric acid	14·55
Sulphuric acid	trace
Chlorine	0·81
Silica	4·35
Carbonic acid	24·30

If much more than 4 p.c. of oxide of iron be detected, it indicates adulteration by the addition of iron filings or magnetic oxide of iron.

The following results were obtained in the Inland Revenue Laboratory (J. Bell):—

—	Congou (low)	Congou (fine)	Hyson	Souchong	Moning	Assam	Gunpowder (fine)
Total ash on dry tea . .	6·10	6·94	6·46	5·99	8·29[1]	6·49	6·67
Sand	3·08	8·51	2·17	1·51	13·37	3·72	5·66
Silica	6·35	9·27	5·93	3·77	9·47	2·51	6·52
Chlorine	1·06	1·07	1·12	1·01	0·99	0·97	1·11
Potassium, to satisfy chlorine	1·16	1·17	1·23	1·11	1·09	1·07	1·22
Potash, K_2O	34·38	28·87	35·66	34·29	26·83	37·71	30·69
Soda, Na_2O	0·62	1·07	0·80	0·34	0·50	0·97	1·27
Ferrous oxide, FeO . .	2·82	0·84	1·12	1·68	2·23	0·57	1·43
Alumina, Al_2O_3 . . .	5·55	3·42	2·73	4·19	4·52	1·54	2·70
Manganese oxide, Mn_3O_4 .	1·68	1·37	1·93	1·59	1·49	2·11	1·92
Lime, CaO	8·82	8·74	9·54	8·98	9·04	8·58	8·19
Magnesia, MgO . . .	2·12	4·87	4·65	3·19	2·42	6·48	6·52
Phosphoric anhydride, P_2O_5 .	14·11	14·68	14·11	18·54	12·69	14·74	16·15
Sulphuric anhydride, SO_3 .	6·52	6·54	6·34	6·38	5·39	5·83	6·68
Carbonic anhydride, CO_2 .	11·73	9·58	12·67	13·42	9·97	13·20	9·94

[1] Moning ash very high 'arising from sand and silica.' Less in another analysis.

A determination of the amount of ash alone may serve to detect the presence of leaves other than those of the tea plant, for these usually differ largely from tea leaves in the amount of their ash. Paraguay tea, however, contains about the same amount of ash as true tea, but differs in the proportion of soluble and insoluble ash.

	Soluble	Insoluble	Total
Common tea . .	3·55	2·37	5·92
Paraguay tea . .	4·22	2·06	6·28

Almost the whole of the insoluble portion of the ash dissolves in hydrochloric acid; any residue is probably sand.

Warington found from 34 p.c. to 45·5 p.c. ash in '*Lie*-teas,' and from 4·73 p.c. to 6·5 p.c. in true teas.

Very little is known about the *oil of tea*, which is supposed to give it its flavour. It is of a lemon-yellow colour, lighter than water, solidifies easily with cold, and resinifies on exposure to air. It has a strong smell like that of the tea plant. It appears to be formed during manufacture, and it is possible that more than one kind of oil is produced. It is probably a narcotic. There is about 0·5 p.c. oil in black tea, and 1 p.c. in green. New tea contains more than old.

The highest amount of *moisture* known in air-dried tea is 16 p.c. According to Wigner, the mean of the amounts yielded by driest Hysons and gunpowders and the moistest Congous is 7·67 p.c. Dragendorff found the average amount of moisture in twenty-three teas of Russian commerce to be 10 p.c. Péligot gives the amount in black tea as 10 p.c.; in green tea as 8 p.c. W. M. Green found in Assam tea 7·76 p.c. moisture.

The *nitrogen* often comes from the albumen and theine.

Péligot gives	6·5 p.c.
Hodges (average of four teas) .	3·93
Wigner (do. do.) .	3·52
W. M. Green	3·37

Gluten or *legumen* forms a quarter of the weight of the leaves according to Johnstone and Church ('Chemistry of Common Life'); but as it is hardly soluble in water, it is of no practical dietetic value. More will be dissolved if soda be added to the water. The 'brick tea' used in Thibet is prepared in such a way as to extract the greater part of the gluten; the tea is rubbed to fine powder, and boiled in the alkaline steppe-water with salt and butter, or fat of some kind, and the infusion is then poured off. This tea is extremely nutritious, and, mixed with a little milk, forms the food of the inhabitants for weeks at a time. One of the Himalayan tribes, and some other tea-drinkers, eat the leaves after drinking the infusion, thus getting the whole of the nutriment.

Tea infusion. Of the matter *extracted by water* from tea we have the following particulars.

From experiments made in the Laboratory of the Inland Revenue, Bell obtained the following amounts of *total extractive matter by water*:

Chinese teas.

Pekoe leaves . . .	54·0 p.c.
Pekoe Souchong . . .	52·3

Indian teas.

Pekoe leaves . . .	48·9 p.c.
Pekoe Souchong . . .	49·3

Eder determined the proximate principles of tea infusion with the following results:

	Dissolved by water	Remained in leaves
Dry matter . .	40·0 p.c.	60·0 p.c.
Nitrogenous substances . .	12·0	12·7
Theine. . .	2·0	—
Tea oil. . .	0·6	—
Resin, chlorophyll, &c. . . .	—	7·2
Tannin . .	10·0	—
Extractive matter	12·0	10·0
Ash . . .	1·7	2·3
Potash. . .	0·938	0·29
Lime . . .	0·036	0·584
Phosphoric acid .	0·133	1·031
Silica . . .	0·021	0·68

O. Kellner, in conjunction with S. Ishii and M. Kamoshita, determined the proportions of the constituents of tea in the *infusions ordinarily drunk* in Japan. The methods of making the infusions are, however, different from those employed in this country. They are:

1. For tencha, extra-fine green tea, the leaves are ground to powder, and drunk with the infusion.
2. For superior green tea, the leaves are digested for two minutes with water at a temperature of 50–60°C.
3. For medium green tea, boiling water is poured on the leaves, and stands on them for one minute.
4. For inferior tea, the leaves are boiled with water.

The object in all these methods is to get out as much theine and oil as possible, together with a moderate amount only of tannin.

Kellner digested 90 grms. superior green tea with half a litre of distilled water at 50°C. After five minutes the infusion was poured off, and another half-litre of water at 50°C. was added to the leaves. This was repeated three times, and each infusion was analysed separately, with the following results:—

—	In 100 grms. of tea employed	In first infusion	In second infusion	In third infusion
	grms.	grms.	grms.	grms.
Dry matter	88·60	4·69	4·17	3·16
Theine	3·43	0·50	0·41	0·42
Tannin	15·75	2·50	2·26	2·20
Total nitrogen	6·541	0·292	0·267	0·251
Ash	5·14	0·88	0·74	0·25
Ash ingredients.				
Potash	1·996	0·297	0·296	0·120
Soda	0·297	0·085	0·175	0·027
Lime	0·132	0·006	0·005	0·008
Magnesia	0·612	0·068	0·037	0·032
Ferric oxide	0·437	0·020	0·005	0·002
Mangano-manganic oxide	0·065	0·017	0·003	0·002
Phosphoric acid	0·921	0·065	0·036	0·028
Sulphuric acid	0·499	0·103	0·022	0·020
Silica	0·077	0·038	0·009	0·006
Chlorine	0·129	—	—	—

Percentage amount of each constituent dissolved.

—	First infusion	Second infusion	Third infusion	Total
Dry matter	5·3	4·7	3·6	13·6
Theine	14·6	12·0	12·3	38·9
Tannin	15·9	14·4	13·9	44·2
Total nitrogen	5·2	4·7	4·4	14·3
Ash	17·1	14·4	4·9	36·4
Ash ingredients.				
Potash	15·1	15·1	6·1	36·3
Soda	28·6	58·9	9·1	96·6
Lime	4·6	3·8	2·3	10·7
Magnesia	11·1	6·0	5·2	22·3
Ferric oxide	4·6	0·1	0·05	4·75
Mangano-manganic oxide	26·2	4·6	3·1	33·9
Phosphoric acid	7·1	3·9	3·0	14·0
Sulphuric acid	20·8	4·4	4·0	29·2
Silica	49·4	11·9	8·1	69·4

Thus the three infusions have much the same composition, but a fourth infusion would probably be different, for it has very little 'body' or aroma.

The boiling-water method gives different results. Kellner digested 100 grms. of superior[1] tea with 1 litre boiling distilled water, and the first infusion contained more than the sum of the contents of the three infusions by the warm-water method. The following table shows his results:

—	In 100 grms. of tea employed	In the total infusion	From 100 parts of each constituent the following parts were dissolved
	grms.	grms.	grms.
Dry matter	95·52	15·34	16·1
Theine	3·31	1·33	40·1
Tannin	19·10	7·04	36·8
Total nitrogen	6·19	1·061	17·1
Ash	5·92	2·14	36·1
Ash ingredients.			
Potash	3·195	1·384	43·8
Soda	0·307	0·101	32·1
Lime	0·572	0·034	6·0
Magnesia	0·359	0·142	39·4
Ferric oxide	0·204	0·022	10·8
Mangano-manganic oxide	0·098	0·050	51·0
Phosphoric acid	0·579	0·233	40·2
Sulphuric acid	0·326	0·080	24·5
Silica	0·186	0·004	2·1
Chlorine	0·127	0·069	54·3

Table showing general results of above comparison of infusions.

In 1 litre	Warm water				Boiling water
	First infusion	Second infusion	Third infusion	Average	
	grms.	grms.	grms.	grms.	grms.
Dry matter	8·43	7·60	5·69	7·24	15·34
Theine	0·91	0·74	0·75	0·80	1·33
Tannin	4·49	4·07	3·97	4·18	7·04
Crude protein	0·528	0·476	0·452	0·486	1·061
Nitrogen free extract	1·82	1·83	0·82	1·29	5·08
Total ash	1·59	1·33	0·45	1·29	2·11
Potash	0·535	0·533	0·216	0·428	1·384

W. M. Green made similar researches on infusions prepared according to the English method. 420 cm. boiling distilled water were poured on to 3·5 grms. tea, a cosy was put on to the tea-pot, and the tea was digested for a given number of minutes, with results as follows:—

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[1] In practice, it must be remembered, only inferior teas are brewed in this way. Thus the results will be higher than is practically the case.

—	5 minutes' infusion per cent.	10 minutes' infusion per cent.	20 minutes' infusion per cent.	40 minutes' infusion per cent.
Extractive matter by water .	21·78	25·35	26·81	28·14
Theine	1·11	1·30	1·16	—
Tannin	6·85	8·52	11·73	16·32
Nitrogen	1·11	1·16	1·11	1·04
Ash	3·52	4·09	4·15	4·48

A strong decoction of tea frequently becomes turbid on cooling, and is covered by a thin pellicle, caused by separation of tannate of theine. This would account for the fact that there is less theine and less nitrogen in the 20 minutes' than in the 10 minutes' infusion. After 40 minutes the temperature of the water had fallen from 100°C. to 60°C.

W. Dittmar has determined the amounts of theine and tannin in solution after (1) five minutes' and (2) ten minutes' infusion of a number of Chinese, Ceylon, and Indian teas, with the following average results, expressed in per cents. of tea:—

—	—	Theine	Tannin	Ratios	
				Theine	Tannin
Chinese, 8 samples . .	5 minutes	2·58	3·06	1	1·18
	10 ,,	2·79	3·78	1	1·35
Ceylon, 6 samples . .	5 ,,	3·15	5·87	1	1·86
	10 ,,	3·29	7·30	1	2·21
Indian, 12 samples . .	5 ,,	3·63	6·77	1	1·86
	10 ,,	3·73	8·09	1	2·16

The following determinations were made on samples of choice Ceylon Pekoe Tips after *ten minutes'* infusion:

	Per 100 parts of tea	
	Theine	Tannin
'Heatherset,' sold at 1*l*. 10*s*. per lb. .	3·15	6·63
'Havillant,' sold at 17*l*. per lb. .	3·40	7·47

In the preparation of the five minutes' infusions, 10 grms. of the tea were digested with half a litre of boiling water in a flask surrounded by cotton wool; after three minutes' standing the contents of the flask were shaken, and after standing five minutes were filtered through muslin into a half-litre flask, the residual leaves being washed with a small quantity of water and the washings added to the main portion. After cooling the infusion was made up to exactly 500 c.c., and the theine and tannin determined in aliquot portions; the former by the magnesia and chloroform method, the latter by Löwenthal's method. The ten minutes' infusions were prepared in an exactly similar manner, except that the contents of the flask were agitated after five minutes' standing, and filtered after ten minutes' standing.

These results show that practically no more theine is extracted by ten minutes' infusion than by five minutes' infusion, but that the amount of tannin is considerably increased by the longer infusion. They also show that Indian and Ceylon teas contain slightly more theine, and considerably more tannin, than China teas.

Tea infusion always grows blacker as it stands. This is probably due to the increase of tannin in the solution and its alteration by oxidation.

With regard to infusions of tea, it should be remembered that different results are obtained from the same tea, according to whether the water used is hard or soft. The larger wholesale dealers have analyses made of the waters used in the different towns and districts which they supply, and sell different teas in different neighbourhoods, the kind depending on the particular water used in each.

Adulteration in its old forms is very little practised now, probably not at all in this country. But inferior teas from old stocks are sometimes sold, also teas recovered from wrecked vessels and re-dried. These generally contain a very large percentage of common salt.

The modes of adulteration formerly common were:—

1. Adding leaves of different kinds, as beech, hawthorn, *Camellia Sasanqua*, sloe, willow, &c., also tea leaves that had been already used.
2. 'Facing' black tea with graphite.
3. Adding colouring matters to green tea, notably indigo or a mixture of Prussian blue and gypsum.
4. Adding catechu and other astringent principles.
5. Adding sand containing ferric oxide to increase the weight of the tea.

The above adulterations were detected both by the microscope and by analysis of the ash, and in the case of foreign leaves, or leaves already infused, by determining the amount of theine and tannin.

A regular form of 'lie-tea' made in China was the sweepings of tea-warehouses, cemented by rice-water and rolled into grains. As much as 500,000 lbs. of such tea has been sent in one year to England.

Different plants are used as tea in different parts of the world. The chief of these is the *Ilex paraguayensis*, or Brazilian holly, whose leaves make what is known as Paraguay tea or 'maté.' It contains a narcotic *volatile oil*, the quantity of which soon decreases when the tea is kept; 2 p.c. *theine*, according to Stenhouse (probably more); 16 p.c. *astringent acid*, analogous to tannin, and which blackens on exposure to the air; 10 p.c. gluten. The total extractive matter is 25 p.c. This tea infusion has been drunk by the Indians from time immemorial. All classes in Paraguay have drunk it for 300 years; and it is now taken by almost the whole population of South America. The Creoles drink it before every meal. Its aroma resembles that of our tea, and it has a pleasant bitter taste. It is said to be more exciting than our tea, and to produce delirium tremens if taken in excess. The leaves are sometimes eaten after the infusion has been drunk. Two other species of holly are used for tea in Brazil; and teas drunk in Chili and in Central America, and called Paraguay tea, are prepared respectively from *Psoralea glandulosa* and *Capraria biflora*.

Other plants whose leaves are used to make tea are:—

Coffee-tree.

Glaphyria nitidia (a species of myrtle), in the Eastern Archipelago.

Ledum palustre and *Ledum latifolium* make 'Labrador tea.'

Catha edulis makes 'Abyssinian tea,' known as 'Kât' or 'Kaat.'

Various species of *Melaleuca* and *Leptospermum* (belonging to the myrtle order), various species of *Correa* (belonging to the *Rutaceæ*); *Acæna sanguisorba* (allied to the *Rosaceæ*), and the *bark* of the Australian *Sassafras*, make the 'Abyssinian tea' of Australia and Tasmania.

Angræcum fragrans (an orchid) makes the 'Faham tea' of Mauritius.

All the above teas, except the last, contain *theine*, and all have a volatile oil and an astringent principle allied to tannin.

For further particulars respecting them and other teas *v.* Church and Johnstone's 'Chemistry of Common Life.' W. M. G.

TELÆSCIN *v.* Horse-chestnut.

TELLURITE *v.* Tellurium.

TELLURIUM. Sym. Te. At. wt. 127·7 (Wills, v. Hauer, Berzelius), 127·64 (Brauner).

Tellurium rarely occurs in the free state; in Colorado crystals have been found containing 99·9 p.c. of tellurium, with traces of gold, silver, and copper. It occurs in small quantities as *tellurite* or *tellurium ochre* TeO_2, *graphic tellurium* or *sylvanite* $(AgAu)Te_3$, *black tellurium* or *magyagite* $(AuPb)_2(TeS.Sb)_3$, *white tellurium* Ag_2Te, and *tetradymite* Bi_2Te_3. It also occurs in arsenical iron pyrites, and is found in the seleniferous mud of the sulphuric acid chambers. Egleston has observed its presence in 'red short' copper.

Crystalline tellurium is a bluish white, metallic-looking, brittle solid of sp.gr. 6·24, melting at 455° (Carnelley a. Williams). The vapour density of its vapour is normal at 1390° (Deville a. Troost).

Tellurium, like selenium, exists in the amorphous and crystalline conditions, the conversion of the former into the latter *absorbing* heat. It burns with a blue flame, is insoluble in water and carbon bisulphide, but dissolves in cold fuming sulphuric acid, with deepened colour and production of tellurium sulphoxide $STeO_3$, from which tellurium is precipitated on addition of water.

When tellurium is heated with hydrogen, or when zinc telluride is treated with hydrochloric acid, the hydride TeH_2 is produced. When heated, this gas is again reduced to crystalline tellurium and hydrogen. It dissolves in water, and precipitates heavy metals as tellurides.

Tellurium forms three oxides, TeO, TeO_2, and TeO_3, tellurous and telluric acids and their salts, corresponding to the latter oxides, and two sulphides, TeS_2 and TeS_3. Two chlorides, $TeCl_2$ and $TeCl_4$, and the corresponding compounds with bromine and iodine, and a tetrafluoride, are also known.

The high atomic weight obtained for tellurium by Wills, v. Hauer, and Berzelius, and confirmed by the laborious analyses of Brauner, would render it impossible to place that element in the position assigned to it by the periodic law which requires that tellurium should have an atomic weight lying between those of antimony and iodine. From analyses of the tetrabromide and dibromide, and from observations regarding those compounds, however, Brauner considers that the tellurium hitherto known consists of a mixture of tellurium with unknown elements. He has succeeded, by fractional precipitation of tellurium solutions, in obtaining a number of new bodies, some of which appear to contain new elements. One of these, which has been named *Austriacum* (*Austrium*) by Brauner, appears to be the *dvi-tellurium* predicted by Mendeléeff. Another body, apparently allied to arsenic and antimony, has also been found (C. J. 1889, 382; and C. J. Abs. 1889, 94).

TELLURIUM OCHRE *v.* Tellurium.

TEMPER. An alloy of arsenic and lead sometimes used for hardening shot, *v.* Arsenic, alloys of; also, Tin.

TENNANTITE *v.* Fahl-ore.

TERBERITE *v.* Tungsten.

TERBIUM *v.* Cerium metals.

TEREBENE *v.* Oils, essential.

TERPENES. The essential or volatile oils which are so widely diffused through the vegetable kingdom consist, with comparatively few exceptions, of hydrocarbons, terpenes, having the formula $C_{10}H_{16}$, together with products which have probably been formed from them by polymerisation or oxidation. The turpentine oils obtained from the wood, leaves, or fruits of various conifers, the essences of lemon, bergamot, orange, and other fruits of the natural order *Aurantiaceæ*, the essential oils extracted from the leaves and flowers of many of the *Labiatæ*, and from the fruits of the *Umbelliferæ*, are among the most important, but many other plants yield volatile oils of similar character (*v.* Oils, volatile).

The terpenes are liquids (b.p. 156–176°) of characteristic odour, not sensibly soluble in water, though they communicate to it their peculiar taste and odour, miscible with strong spirit of wine, but usually in limited quantity, miscible in all proportions with glacial acetic acid. The terpenes existing in nature are all optically active, some being dextro- and others lævorotatory. No homologues are at present known, the composition C_9H_{14} attributed to a product of distillation of podocarpic acid described by Oudemans (B. 6B, 1125) resting on insufficient evidence.

Before 1876 it was known that the terpene from essence of lemon boils at a temperature nearly 20° higher than the b.p. of oil of turpentine, but no classification of the terpenes had been attempted. Tilden and Shenstone then prepared the nitrosochlorides (C. J., May 1877), and from a study of these compounds divided the known terpenes into three classes (Tilden, C. J. Feb. 1878), as follows:—

1. Turpentines, or terpenes proper (156–160°).
2. Citrenes (174–176°).
3. Sylvestrene (173–175°), discovered by Atterberg (B. 10B, 1202).

Since that date the most important systematic experiments are those of O. Wallach (A. 225, &c.).

Disregarding for the present the solid camphenes and the polyterpenes, the following additional groups must now be recognised:—

4. Dipentene (175–176°) (Wallach).
5. Terpinolene (185–190°) (Wallach).
6. Terpinene (about 180°) (Wallach).
7. Phellandrene (about 170°) (Pesci, Gaz. Chim. Ital. 16, 225).
8. Fenchene (158–160°) (Wallach, A. 263, 129).

In the following account of these compounds the names which have been introduced by Wallach are employed:—

1. **Pinene group** (= turpentines or terpenes proper).

Australene, or dextro-pinene, of which rectified American turpentine, from *Pinus australis* and *P. Tæda*, almost wholly consists, is obtained by agitating the commercial oil with an alkaline solution, drying completely, and carefully fractionating (156°). Dextrorotatory $[\alpha]_j = +21{\cdot}5$ (Berthelot, A. 83, 105; 88, 345, 110, 367; Suppl. ii. 226). $[\alpha]_D = +25{\cdot}9$, $D\,\frac{0}{4} = {\cdot}8765$, $D\,\frac{25}{25} = {\cdot}8586$, $D\,\frac{100}{100} = {\cdot}8278$ (Tilden, unpublished experiments). This compound is also a constituent of many volatile oils, *e.g.* Russian and Swedish turpentine oils, from *Pinus sylvestris* and *P. Ledebourii* (Tilden, C. J. 33, 80); wormwood and spearmint (Brühl, B. 21A, 156).

Terebenthene or lævopinene. French turpentine oil, from *P. maritima*, consists chiefly of this hydrocarbon. (156·5°). $[\alpha]_j = -40{\cdot}32$. $D\,\frac{0}{0} = {\cdot}8767$, $D\,\frac{17{\cdot}88^\circ}{17{\cdot}88^\circ} = {\cdot}8619$ (Riban, C. R. 78, 788; 79, 314). Present also in oil of rosemary (Bruylants, J. 1879, 944), oil of lemon (Tilden, Ph. [3] 9, 654), sage and juniper (C. J. 31, 554), thyme and anise (Brühl, B. 21A, 156), and others.

For production and properties of turpentine oils *v.* OILS, ESSENTIAL.

Both dextro- and lævo- rotatory pinenes from different sources differ considerably in rotatory power, the hydrocarbon from juniper, for instance, giving a rotation of only about 1° for a column of 100 mm. (Tilden a. Shenstone, C. J. 1877, i. 557). To what cause this is due has not been determined, but it is suggested by Armstrong that in the case of American turpentine the low dextrorotatory power is due to the presence of a lævorotatory terpene. All agree, however, in the following chemical characters. Dry hydrogen chloride gas unites with the hydrocarbon, forming a monohydrochloride $C_{10}H_{16}HCl$ [125°] (*v. Camphene, infra*); in the presence of water, alcohol, ether, or acetic acid, hydrogen chloride forms a dihydrochloride $C_{10}H_{16}2HCl$ [50°] (*v. Dipentene, infra*); nitrosylchloride gas passed into a solution of the terpene in chloroform at −10° forms a nitrosochloride $C_{10}H_{16}NOCl$ [103°] (Tilden, C. J. 1875, 514 and 1877, i. 554), the same compound being formed by the action of hydrogen chloride on a cooled mixture of the terpene with amyl nitrite and glacial acetic acid (Wallach, A. 245, 245). The nitrosochloride treated with alcoholic potash yields a nitroso- compound $C_{10}H_{15}NO$ [131°]. (For crystallography, *v.* N. Story-Maskelyne, C. J. 1875, 518 and Phil. Mag. 1879, 129.) Mixed with alcohol and nitric acid, pinenes yield crystallised terpin hydrate $C_{10}H_{20}O_2.OH_2$ (Wiggers, A. 33, 358; 57, 247; Tilden, C. J. 33, 247; Hempel, A. 180, 71). When exposed to air or oxygen in the presence of sunlight the pinenes yield an interesting crystalline product $C_{10}H_{18}O_2$, discovered by Sobrero (C. R. 33, 66). Armstrong proposes to call this compound, which is an alcoholic body, *Sobrerol*. When distilled with dilute acid it yields a compound, *Sobrerone*, which is identical with one of the products of the action of nitrous acid upon pinene isolated by Wallach and Otto, and called by them *pinol* (A. 253, 249). Sobrerol is dextro- or lævo- rotatory according to the character of the terpene from which it is formed. The pure substance melts at 150°, but when equal weights of the two varieties are mixed an inactive compound is obtained which melts at 131° (Armstrong and Pope, C. J. 59, 311).

2. **Limonene group** (= citrenes).

Dextro-limonene (174–176°), D ·846 at 20°. When obtained from oil of orange $[\alpha]_D = +106{\cdot}8$ *ca.* (Wallach, A. 252, 145). This hydrocarbon constitutes the chief ingredient in oils of orange, bergamot, lemon, and limes; it is also present in oils of carraway, pine needles (*P. sylvestris* ?), dill, erigeron, &c.

Lævo-limonene is contained in the oil of Scotch fir leaves (*P. sylvestris*), sometimes called 'Fir-wool oil' (Tilden, C. J. 33, 83; Wallach, A. 227, 287). A specimen, believed to have been obtained from leaves of *P. picea*, gave (175–176°), $D\,\frac{20}{20} = {\cdot}846$, $[\alpha]_D = -105^\circ$ (Wallach, A. 246, 221).

The limonenes are distinguished by giving with hydrogen chloride a liquid monochloride and a dihydrochloride [50°] identical with that obtained from the pinenes; also a nitrosochloride, either by the direct addition of nitrosylchloride (Tilden a. Shenstone) or by action of amyl or ethyl nitrite and hydrochloric acid (Wallach). From the nitrosochloride is obtained a nitroso- compound [71°] which, when prepared from *lævo*-limonene, is identical in every respect with carvoxim $C_{10}H_{14}N.OH$ from carvol. (For Crystallography, *v.* N. Story-Maskelyne, P. M. 1879, 132; for a comparison of the rotatory powers of the two limonenes and their derivatives, *v.* Wallach, A. 252, 141.) The limonenes are further characterised by the formation of a crystalline tetrabromide $C_{10}H_{16}Br_4$ [104–105°], by direct addition of bromine (Wallach, A. 227, 277).

It appears from Wallach's later researches that the nitrosochloride obtained as described above either from dextro- or lævo- limonene is always a mixture of two compounds, which are separable from each other by means of cold chloroform in which the *α* compound is more soluble than the *β*. The former crystallises from ether in large clear crystals, the latter in needles. There is a slight difference of melting-point, and the *α* compound has in each case a greater rotatory power than the *β*, but the two nitrosochlorides seem to be only physical isomerides, and are chemically identical, as they yield exactly the same derivatives (A. 252, 113). This point, however, requires further investigation.

3. **Sylvestrene**, in Swedish turpentine, obtained by dry distillation of fir wood (Atterberg, B. 10, 1206); also in Russian turpentine (Tilden, C. J. 33, 80; Wallach, A. 230, 245), in company with australene (176–177°), D $\frac{16}{16}$ = ·8510, D $\frac{20}{20}$ = ·8470, $[\alpha]_D = 66{\cdot}32°$ (Wallach, A. 245, 197). The odour of sylvestrene is different from that of common turpentine, and resembles the odour of fresh fir wood. It forms a liquid monohydrochloride and dihydrochloride [72°], from which the hydrocarbon may be recovered unchanged by heating with aniline and alcohol. Sylvestrene yields a nitrosochloride [106–107°], which is strongly dextrorotatory, and by decomposition with alcoholic potash gives an oily product. It also yields a tetrabromide [135°] crystallising in monosymmetric tables (A. 239, 29).

4. **Dipentene.** This name includes diisoprene (*v.* Pentylenes, Watts' Dictionary of Chemistry, vol. iii.), isoterebenthene, formed by the action of heat on terebenthene, cinene, cajeputene, caoutchene (*q. v.*). Dipentene is produced, together with terpinene, terpinolene, and terpineol by the action of sulphuric or phosphoric acid on terpin, or by the action of sulphuric acid on the pinenes under certain conditions. The product thus obtained was formerly called 'terpilene.' Dipentene may be prepared from the dihydrochloride [50°] obtained from either limonene or moist pinene, by the action of heat on the chloride (Tilden, B. 12, 1133), or by boiling it with a mixture of sodium acetate and acetic acid, or with alcohol and aniline (Wallach). Dipentene thus obtained is, however, accompanied by considerable quantities of cymene, terpinene, terpinolene, together with a small amount of a saturated hydrocarbon of boiling-point 155° (Tilden, C. J. Feb. 1893). The foregoing methods are all artificial; the only natural products in which dipentene is known to exist are the volatile oils of the camphor tree (Wallach, A. 227, 296), also oil of elemi, and in Russian and Swedish turpentine (Wallach).

Dipentene boils at 175–176°. It has a pleasant smell of lemons, it combines with bromine, forming a tetrabromide [125–126°], and unites with 2HCl, forming a compound [50°], identical with the dihydrochloride obtained from pinene.

The nitrosochloride [101 102°] yields by the action of alcoholic potash an inactive carvoxim [92–93°]. Dipentene also gives a nitrosonitrate $C_{10}H_{16}NO.ONO_2$ [84°] (A. 245, 367).

Dipentene is optically inactive, and may be produced synthetically by mixing together equal quantities of dextro- and lævo- limonene, just as racemic acid may be formed by intermixture of dextro- and lævo-tartaric acids. The compound in this case, however, appears to differ so decidedly from limonene that dipentene has hitherto been regarded as a distinct hydrocarbon. The derivatives of dipentene are also inactive, and may be formed by union of the corresponding limonene compounds.

Thus the inactive isonitroso-dipentene or carvoxim [93°] may be formed by mixing together equal quantities of the lævocarvoxim [72°] from dextrolimonene, and dextrocarvoxim [72°] from lævopinene. The compound which results, notwithstanding the difference of m.p., still gives by Raoult's method a molecular weight corresponding to the simple formula $C_{10}H_{15}NO$ (Wallach, A. 246, 230).

It appears that certain derivatives of dipentene exist in a second optically inactive form.

When pure *α* limonene nitrosochloride (*v. Limonene*), prepared from either dextro- or lævo-limonene, is warmed with an alcoholic solution of piperidine, a mixture of two crystallisable nitrolamines results in each case, as follows:

α. Nitrolpiperidines $C_{10}H_{16}NONC_5H_{10}$.

From lævolimonene.

α. [93–94°]. Rhombic (from alcohol). $[\alpha]_D = -67{\cdot}60°$. Hydrochloride *dextro-* rotatory.

β. [110–111°]. Monosymmetric. $[\alpha]_D = +60{\cdot}18°$. Hydrochloride almost inactive.

From dextrolimonene.

α. [93–94°]. Rhombic. $[\alpha]_D = +67{\cdot}75°$. Hydrochloride *lævo-* rotatory.

β. [110–111°]. Monosymmetric. $[\alpha]_D = -60{\cdot}48°$. Hydrochloride?

Similar results have been obtained by the employment of aniline and benzylamine. The salts of the bases thus produced possess in every case a rotatory power opposite in direction to that of the base from which each is derived.

From the foregoing statement it is clear that from each of the two active modifications of limonene two distinct series of bases are derived. Two other series may be formed from the inactive hydrocarbon. Thus when the two *α* piperidine bases [93–94°] above described are dissolved in petroleum spirit, and the solutions mixed, an inactive nitrolamine [154°] is at once precipitated. A second inactive compound [152°] is formed in like manner by mixing the *β* limonene bases (Wallach, A. 252, 123). The question whether all dipentene compounds are capable of existing in two modifications remains to be settled. Wallach has observed (A. 239, 13–14) that the hydriodide formed from cineol, or from terpin hydrate, crystallises in two different forms with a slight difference of melting-point—viz. rhombic [77°], monosymmetric [78–79°]. At present, however, no method is known of producing from limonene active addition compounds with two molecules of hydracid; with excess of hydrogen chloride, for example, the same inactive dipentene hydrochloride [50°] is obtained.

Dextrolimonene and lævolimonene give when oxidised no toluic or other benzenoid acid, but dipentene, when made from the dihydrochloride, gives about one-third of its weight of paratoluic acid. This, however, is due to the presence of cymene and terpinene. Pure dipentene may be obtained from the products of destructive distillation of india-rubber (*v. Caoutchin*, vol. ii. 311). This liquid when oxidised yields the same products as limonene (C. J. 53, 879, and Feb. 1893).

5. **Terpinolene** (185–190°). The formation of this hydrocarbon has already been referred to, § 5. It forms an optically inactive tetrabromide, which crystallises in monosymmetric tables [116°], and is quite distinct from the tetrabromides of dipentene and limonene, especially in its instability, the crystals becoming gradually converted into a porcelain-like opaque mass.

With hydrogen chloride and hydrogen bromide terpinolene unites to form the dipentene hydrochloride [50°] and hydrobromide [64°], in this respect resembling limonene.

6. **Terpinene**. The product obtained by boiling terpin hydrate with diluted sulphuric acid (Tilden, C. J. 33, 250), that formed by the action of slightly-diluted sulphuric acid on turpentine (Armstrong a. Tilden, C. J. 35, 747), also the product of heating the dihydrochloride $C_{10}H_{18}Cl_2$ [50°], were formerly believed to be identical, and received the name terpinylene or terpilene (Berthelot).

The action of sulphuric or phosphoric acid on terpenes and on terpin is now known to yield, in addition to products of polymerisation (colophene), three distinct hydrocarbons—namely, dipentene, already described (175–176°), terpinene (179–181° *ca.*), and terpinolene (185–190°) (Wallach).

Terpinene has not been obtained in an absolutely pure state, but is well characterised by the formation of a nitrosonitrite $C_{10}H_{16}N_2O_3$ [155°] (Wallach, A. 239, 33).

The tetrabromide is fluid, and it yields no crystallisable hydrochloride. A hydrocarbon of like properties has been found in oil of cardamoms (Ev. Weber, A. 238, 98).

Terpinene-nitrosonitrite by the action of bases is converted into nitrolamines, for example:

$$C_{10}H_{15}\left<\begin{matrix}NOH\\NH_2\end{matrix}\right> [116\text{–}118°],$$

$$C_{10}H_{15}\left<\begin{matrix}NOH\\NHC_2H_5\end{matrix}\right> [130\text{–}131°]$$

(Wallach, A. 241, 315).

7. **Phellandrene** (Pesci, G. 16, 225). The seeds of *Phellandrium aquaticum* contain about 2·5 p.c. of a volatile oil, of which about 80 p.c. consists of a dextrorotatory terpene (171–172°). The same hydrocarbon is contained, together with anethol, in the oil of bitter fennel, *Fœniculum vulgare* (Wallach, A. 239, 40). It also forms a constituent of oil of elemi.

In the oil of *Eucalyptus Amygdalina* Wallach finds the isomeric lævo- phellandrene (A. 246, 232).

Phellandrene in either form is easily alterable by the action of acids into dipentene and terpinene; also into a solid polymeride $C_{20}H_{32}$ [86°].

Phellandrene is specially characterised by the formation of a nitrosonitrite $C_{10}H_{16}.N_2O_3$, first observed by Cahours, afterwards (Z. 1869, 579) examined by Bunge. Pesci obtained it by the action of a nitrite and dilute sulphuric acid upon the hydrocarbon. It forms long silky needles [94°], and although obtained from the dextro- variety, rotates the plane of polarisation to the left $[\alpha]_D = -183{\cdot}5°$ (Pesci).

By reducing agents this compound is converted into a base $C_{10}H_{16}(NH_2)_2$ (209–214°), and by ammonia into nitrophellandrene $C_{10}H_{15}NO_2$ and an acid.

Phellandrene is easily changed by contact with hydrobromic acid into dipentene, and by boiling with alcoholic sulphuric acid it is converted into terpinene.

8. **Fenchene.** A liquid isomeride of camphor (190–193°) can be separated from oil of fennel, and is called by Wallach *fenchone*. By reducing this with sodium and alcohol, it yields the alcohol $C_{10}H_{17}.OH$ as a colourless crystalline compound, from which, by treatment with phosphoric chloride, the compound $C_{10}H_{17}Cl$ is formed. Fenchene $C_{10}H_{16}$ (158–160°) is obtained by heating this chloride with aniline. Fenchene is optically inactive: it differs from other terpenes in being unacted upon by cold nitric acid. Very little is known of this hydrocarbon at present.

Synopsis of terpenes and chief derivatives.

—	Pinene	Limonene	Sylvestrene	Dipentene	Terpinolene	Terpinene	Phellandrene	Fenchene
$C_{10}H_{16}$. approx. b.p.	160°	175°	176°	175°	185–190°	180°	170°	158–160°
$C_{10}H_{16}HCl$ . . m.p.	125°	—	—	—	—	—	—	—
$C_{10}H_{16}2HCl$. m.p.	50° [1]	50° [1]	72°	50° [1]	50° [1] ?	—	—	—
$C_{10}H_{16}Br_4$ . . m.p.	liquid	105°	135°	125°	116°	—	—	—
$C_{10}H_{16}NOCl$. m.p.	103°	103°	106–107°	101–102°	—	—	—	—
$C_{10}H_{16}NO$ . . m.p.	129°	72°	liquid	92–93°	—	—	—	—
$C_{10}H_{16}N_2O_3$ . . m.p.	?	—	—	—	—	155°	94°	—

[1] Identical with dipentene hydrochloride.

Isoterpenes or **Camphenes**. When hydrogen chloride gas is passed into dry turpentine oil, kept cool, it is absorbed, and after a time the liquid solidifies to a crystalline mass of monohydrochloride $C_{10}H_{17}Cl$ [125°] (210°). This compound has long been known, and was formerly described as artificial camphor. If the turpentine is moist, or allowed to become hot, a certain amount of dipentene dihydrochloride is formed, and this, with the monohydrochloride, forms a liquid from which the monohydrochloride can be only partially recovered by fractional distillation or by cooling. The hydrochloride prepared from dextropinene is dextrorotatory, that from lævopinene is lævorotatory. This compound is remarkably stable, but may be decomposed by heating with sodium stearate or benzoate, with potassium acetate, with alcoholic potash, or, according to Wallach, best by a mixture of sodium acetate and caustic soda with alcohol. The resulting hydrocarbon is a camphene [51–52°] (160°), dextro- or lævo- rotatory, or inactive, according to the nature of the hydrochloride used and the reagent employed (Berthelot, C. R. 47, 266, and 55, 496, 544). The exact conditions under which the active camphenes are formed are scarcely known. The inactive compound seems to be produced when a high temperature is used. A camphene is also formed from bornyl chloride (art. CAMPHORS, vol. i. p. 409) by the action of alcoholic potash (Riban), by the action of water and magnesia (Kachler, A. 197, 86), or by heating with aniline to the boiling-point of the latter (Wallach, A. 230, 234). Whether the camphene from bornyl chloride is identical with camphene from pinene is a point which is open to further inquiry (Brühl, B. 25, 166). Camphene is also formed from camphor chloride (vol. i. p. 411) and from pinene hydrochloride by the action of sodium (Montgolfier, C. R. 87, 840):

$$2C_{10}H_{16}2HCl + 4Na = 4NaCl + C_{10}H_{16} + C_{10}H_{20}.$$

In this last case it is accompanied by a liquid hydrocarbon (170°) resembling a paraffin, and possibly identical with a hydrocarbon obtained by the action of concentrated hydrogen iodide on turpentine (Berthelot), also by the action of iodine (Armstrong a. Gaskell, B. 12B, 1756), and by the action of sulphuric acid on turpentine (Armstrong, B. 12B, 1759).

Camphene is also formed, together with other products, by the action of strong sulphuric acid on turpentine, and constitutes the chief ingredient in the liquid formerly known as 'terebene' (Armstrong a. Tilden, C. J. 1879, 745).

Camphene, active or inactive, possesses a characteristic camphoraceous smell, is soluble in alcohol, and crystallises therefrom in leaflets. It combines with hydrogen chloride to form a chloride $C_{10}H_{17}Cl$ [157°], which is distinguished from pinene hydrochloride by its inferior stability (Riban, C. R. 80, 1330; Ehrhardt, C. N. 54, 239).

Camphene hydrochloride is said to be identical with bornyl chloride (Kachler a. Spitzer, A. 200, 340).

Camphene does not combine with bromine, and is attacked by it only slowly, with formation of an oily monobromo- derivative (230–240°). Camphene does not combine with nitrosyl chloride. It is converted at about 300° into liquid products which have not been investigated.

When oxidised by chromic acid, camphene yields camphor, but, according to Marsh and Gardner (C. J. 59, 649), when dilute nitric acid is employed as the oxidant a tribasic acid, $C_{10}H_{14}O_6$, called by them *camphoic acid*, is produced.

Sesquiterpenes $C_{15}H_{24}$. According to Gladstone (C. J. 1872, 1), the oils of clove, calamus, cascarilla, patchouli, and cubebs contain a hydrocarbon of this composition. A sesquiterpene has also been found by Wallach (A. 238, 81) in oils of galbanum and savine and in 'huile de cade,' a kind of tar made by distillation of the wood of *Juniperus Oxycedrus*. According to the latter chemist, the hydrocarbon obtained from cade or cubebs possesses the following properties. It unites with 2HCl, forming a compound which crystallises from ether in large hemihedral rhombic prisms [117–118°], the solution of which is lævorotatory. Heated with aniline or with sodium acetate the hydrocarbon is set free in a pure state (274–275°); $D^{16}_{16} = \cdot921$. The hydrobromide $C_{15}H_{24}2HBr$ melts at 124–125°; the hydriodide $C_{15}H_{24}2HI$ at 105–106°, with partial decomposition. The hydrocarbon, especially when partially resinified by exposure to the air, gives the following characteristic colour reaction: Dissolved in chloroform or glacial acetic acid, and then shaken up with a few drops of strong sulphuric acid, the liquid assumes an intense green and then blue colour, which when heated passes into red.

An attempt to prepare from isoprene a polymeride of the composition $C_{15}H_{24}$ proved unsuccessful (Wallach, *l.c.*).

Conimene, a hydrocarbon $C_{15}H_{24}$ (264°), with a pleasant odour, is obtained from the incense-resin (*Icica heptaphylla*) of British Guiana (Stenhouse a. Groves, C. J. 1876, i. 175).

Polyterpenes $C_{20}H_{32}$ &c. The members of this group may be divided into three classes, viz. (1) Fluid constituents of certain essential oils; (2) caoutchouc and gutta percha; and (3) products of the polymerisation of terpenes.

1. *Oleoresin*, or so-called '*balsam*' *of copaiba* (*Copaifera Langsdorffii* and other species) is a mixture of a resin with an oil which boils at 250–260°. The latter forms with water a hydrate $(C_{20}H_{32})_3H_2O$, which has a peculiar blue colour. The hydrocarbon absorbs hydrogen chloride, with production of a deep-violet colour, but no crystallisable hydrochloride.

A similar oil is obtained from Gurjun balsam or wood oil, the product of various species of *Dipterocarpus* growing in the East.

The least volatile portions of many essential oils contain a hydrocarbon of the same composition.

2. *Caoutchouc*. *V.* INDIA-RUBBER, vol. ii. 311. For further information concerning the products of its decomposition by heat *v.* WATTS' DICTIONARY OF CHEMISTRY (Morley a. Muir), art. PENTYLENES (vol. 3), and *Dipentene* (*supra*), GUTTA-PERCHA, *v.* WATTS' DICTIONARY OF CHEMISTRY, vol. ii. p. 658.

3. *Colophene* is a viscid yellow fluid, often strongly fluorescent, which begins to boil at about 300°. It is produced by exposing oil of turpentine or other terpenes to a temperature of about 300° for some hours, or by the action upon them of concentrated sulphuric or phosphoric acid, phosphoric anhydride, or boron fluoride, &c. The name colophene was given by Deville to the less volatile portion of the product of the action of sulphuric acid on French turpentine, apparently under the impression that it was identical with the oil obtained by distillation of resin. The latter, however, contains oxygen, and exhibits totally different properties.

Colophene obtained by the action of strong sulphuric acid on turpentine oil cannot be distilled without decomposition, even under reduced pressure. The first portions of the distillate contain camphene and dipentene; the boiling-point then rises higher and higher, and even when the temperature approaches that of dull redness a residue is left, which on cooling becomes nearly solid (Armstrong a. Tilden, C. J. 1879, 748). The portions passing over at 300° and upwards appear to consist of saturated compounds, for they absorb mere traces of hydrogen chloride. Riban has obtained from terebenthene, by the action of antimony trichloride, a solid to which he assigns the formula $C_{40}H_{64}$. This is decomposed by heat, and combines with hydrogen chloride to form two compounds,

$C_{40}H_{24}HCl$ and $C_{40}H_{64}2HCl$ (C. R. 79, 389).

Oxidised Compounds related to the Terpenes.

1. **Borneol** $C_{10}H_{17}OH$, *v.* vol. i. p. 409.

2. **Camphor** $C_{10}H_{16}O$, *v.* vol. i. p. 408.

3. **Cineol** $C_{10}H_{18}O$, *v.* vol. i. p. 410.

4. **Terpineol** $C_{10}H_{17}OH$. *Terpinol* was the name given by List to the liquid obtained by the action of dilute acids upon terpin hydrate, but the statements of Wiggers (A. 1846, i. 251), List (A. 1848, 362), and Oppenheim (A. 1864, 149) regarding the composition and properties of this substance are at variance with one another.

The analyses of Wiggers and List indicated the formula $C_{20}H_{34}O$, and List gave the b.p. 168°. The facts are as follows: When crystallised terpin is boiled up in a large quantity of water and a small quantity, say 1 p.c., of hydrochloric acid is added, the crystals disappear and a turbid fluid results, from which by distillation an oily liquid, lighter than water and possessing a peculiar fragrant odour, is obtained. When the oil is dried by calcium chloride and distilled, the whole comes over, with the exception of a few drops at first, between 205° and 215°. A product of perfectly definite boiling-point is not obtainable. Combustion leads to the formula $C_{10}H_{18}O$, and the vapour density found to be 63·8 and 62·3 in two experiments. The formula $C_{10}H_{18}O$ corresponds to a v.d. 77. The compound is therefore partly dissociated by heat into $C_{10}H_{16}$ and H_2O. Treated with sodium, terpineol dissolves one atom of the metal; and by contact with excess of hydrochloric acid it becomes coloured deep purple, but the colour disappears and the whole is converted into dipentene hydrochloride $C_{10}H_{18}Cl_2$ (50°); when mixed gradually with a nearly equal volume of sulphuric acid diluted with half its bulk of water, very little heat is evolved, but solution is complete, and on adding to the mixture three or four volumes of water a mass of crystallised terpin hydrate is obtained. Terpineol is also quickly converted into terpin hydrate by a mixture of nitric acid and alcohol (Tilden, C. J. 1878, 247; 1879, 287).

With carbanil it slowly reacts, forming a crystalline mass of phenyl-terpinyl-methane $NHC_6H_5.CO.OC_{10}H_{17}$ (Wallach, A. 230, 267). Terpineol absorbs two atoms of bromine (Tilden, C. J. 1888, 882), and it is, therefore, an unsaturated monohydric alcohol $C_{10}H_{17}(OH)$, of which the corresponding glycol is terpin $C_{10}H_{18}(OH)_2$. By *boiling* with dilute sulphuric acid terpineol splits into water and terpinene (Wallach, A. 230, 266).

5. **Terpin** $C_{10}H_{18}(OH)_2$ and **Terpin hydrate** $C_{10}H_{18}(OH)_2.H_2O$. This compound is occasionally found in old samples of turpentine oil containing a little water, and in furniture polish of which turpentine is an ingredient. It is easily obtained by the action of a mixture of nitric acid and alcohol upon turpentine oil (Wiggers, A. 1846, 251). Hempel recommends (A. 180, 71) 4 parts oil of turpentine to 1 part of alcohol and 1 part of nitric acid. Tilden uses 2½ measures of turpentine to 1 volume of nitric acid previously mixed with 1 volume of alcohol. In any case, the mixture is shaken up at intervals till in the course of about two days the smell of turpentine has disappeared. The liquid is then poured out into shallow dishes, a little alcohol being added occasionally as long as crystals are deposited (Tilden, C. J. 33, 247). No crystals are formed under the same circumstances from the limonenes, with the exception of dextrolimonene from lemon oil (Tilden, C. J. 34, and Ph. [3] 9, 654). The compound is always the same from whatever source, the crystals agreeing in melting-point [116°–117°], crystalline form, and optical inactivity in alcoholic solution. The crystals have been examined by List (A. 67, 362), by Rammelsberg (P. 63, 570), and by Maskelyne (P. M. 1879, 132).

Exposed to hydrogen chloride gas the crystals deliquesce, become purple, and finally give a mass of the colourless dipentene dichloride $C_{10}H_{18}Cl_2$ [50°]. Boiled with water slightly acidulated with hydrochloric or sulphuric acid it yields terpineol. Boiled with moderately strong sulphuric acid it yields a mixture of dipentene, terpinene, and terpinolene. Terpin is a saturated compound; it has no action upon bromine water.

Action of heat upon the terpenes. When ordinary turpentine oil is passed through a tube heated to redness scarcely visible in the dark, it yields a quantity of gas and various liquid products, of which the most important are isoprene C_5H_8, dipentene $C_{10}H_{16}$, paracymene $C_{10}H_{14}$, and colophene $(C_{10}H_{16})_n$, with relatively small quantities of benzene, toluene, and metaxylene. At higher temperatures no isoprene is obtained, but a larger quantity of gas, and the most volatile liquid product is benzene, which is accompanied by some of its homologues, beside naphthalene, anthracene, &c. (Tilden, C. J. 45, 410).

Limonene (from oil of limes) and dipentene behave very much like turpentine.

Camphene yields other products which have not been examined.

Optical properties of the terpenes. The specific rotatory powers of the several terpenes have been already given; *v.* also Wallach (A. 252, 141). For the specific refractive and dispersive powers of the essential oils and the hydrocarbons contained in them the following papers should be consulted: Gladstone, C. J. 17, 1; 25, 1; 49, 609; Brühl, Zeits. Phys. Chem. 1, 307; B. 21, 457; Wallach, A. 245, 191; Brühl, B. 25, 142, 151, 547.

Chemical constitution of terpenes and their immediate derivatives. Many hypotheses have been brought forward concerning the constitution of these compounds, but they all may be referred to one or other of the two following fundamentally distinct propositions. The terpenes are either aromatic compounds having the composition of hydrides of paracymene, or they consist of closed chains containing ethylenic linkages of carbon to carbon not of the kind which has hitherto been assumed in Kekulé's formula for benzene. As the question is far from being settled, its discussion in detail would not be profitable in this place. The cymene hydride formula was proposed by Oppenheim (B. 5, 94, 628) and supported by Kekulé

(B. 6, 438). Other formulæ have been proposed, and the whole question discussed more recently by Wallach (A. 239, 46; also especially B. 24, 1525), Tilden (C. J. 53, 879), and Collie (B. 25, 1108). W. A. T.

TERRA CATECHU. Syn. with Catechu (*q. v.*).

TERRA DI SIENNA. *Raw Sienna v.* Pigments.

TERRA FOLIATA TARTARI. Potassium acetate.

TERRA JAPONICA. Syn. with Catechu (*q. v.*).

TERRA LEMNIA *v.* Lemnian earth.

TERRA MIRACULOSA. An old name for bole (*q. v.*).

TERRA MURIATICA. An obsolete name for magnesia.

TERRA NOBILIS. Bergmann's name for the diamond.

TERRA PONDEROSA. An old name for baryta (*q. v.*).

TERRA CHE BRUCIA or *Val d'Arno Superiore Resin v.* Resins.

TERRA UMBRA. Umber (*q. v.*).

TETANINE *v.* Vegeto-alkaloids.

TETRADYMITE *v.* Tellurium.

TETRAHEDRITE *v.* Fahl-ore.

TETRAHYDROXYBENZENE *v.* Phenols.

TETRAIODOPYRROLINE *v.* Iodol.

TETRAMETHYLBENZENES *v.* Cymenes.

TETRAMETHYLSAFFRANINE *v.* Azines.

TETRATHIONIC ACID *v.* Sulphur.

TETRYL or **BUTYL**, a univalent radical yielding four isomeric mono- derivatives:

(1) $CH_3.CH_2.CH_2.CH_2X$ (normal);
(2) $CH_3.CH_2.CHX.CH_3$ (secondary);
(3) $(CH_3)_2:CH.CH_2X$ (iso-);
(4) $(CH_3)_3CX$ (tertiary).

Tetryl Compounds.

Tetryl alcohol. Butyl alcohol C_4H_9OH. All the four possible bodies corresponding to this formula are known.

1. *Normal tetryl alcohol.* Propyl carbinol $CH_3.CH_2.CH_2.CH_2OH$; b.p. 116° at 740 mm. (Lieben a. Rossi, A. 158, 137), 117·5° (cor.) (Zander, A. 224, 80), 116·88° (cor.) (Brühl, A. 203, 16); critical temp. 287·1° (Pawlewsky, B. 16, 2634); sp.gr. $\frac{0^\circ}{\;}$ = ·8239, $\frac{20^\circ}{\;}$ = ·8109, $\frac{40^\circ}{\;}$ = ·7994, $\frac{98·7^\circ}{\;}$ = ·7738, $\frac{20^\circ}{4^\circ}$ = ·8099 (B.); $\frac{116·7^\circ}{4^\circ}$ = ·72695 (Schiff, A. 220, 101). Vol. at t° (at 0° = 1) = $1 + ·0_3 8092t + ·0_5 284t^2 - ·0_8 116t^3$ (Z.) $\mu_\beta = 1·4040$; $R_\infty = 35·45$ (B.). Occurs in the heavy oil of Cognac brandy to the extent of 49 p.c. Is not formed in the fermentation of sugar produced by elliptical yeast (Claudon a. Morin, C. J. 52, 714). Is produced by the action of sodium-amalgam upon butyryl chloride and butyric acid (Saytzen, Z. 1870, 108; Linnemann, A. 161, 178). Also by the fermentation of glycerin by *Schizomycetes* and certain other bacteria in presence of calcium carbonate and various foodstuffs, *e.g.* ammonium tartrate; the yield amounts to 9 p.c. of the glycerin used. Butyric acid and a little ethyl-alcohol are also formed (Fitz, B. 9, 1348; Vigna, B. 16, 1348). Is also produced by the action of nascent hydrogen (iron and acetic acid) upon butenyl alcohol (Lieben a. Zeisel, M. 1, 825, 842).

Properties.—Colourless liquid, soluble in 12 parts of water, from which solution it can be separated by means of calcium chloride. Soluble in concentrated hydrochloric acid; is readily oxidised to butyric acid. Fused zinc chloride abstracts water, and yields β-tetrylene and smaller amounts of normal tetrylene (Le Bel a. Greene, Am. 2, 24).

2. *Iso-tetryl alcohol.* Isopropyl carbinol $(CH_3)_2:CH.CH_2OH$; b.p. 106·6–106·8° at 763·2° mm. (Schiff, A. 220, 102), 108·4° (Linnemann, A. 160, 238), 108·5° at 766 mm. (Thomsen, Th. 4, 162), 107·6°–108·3° (cor.) (Perkin, C. J. 45, 421); sp.gr. $\frac{106·6^\circ}{4^\circ}$ = ·7265 (S.); $\frac{0^\circ}{\;}$ = ·8168 (L.); $\frac{15^\circ}{15^\circ}$ = ·8069; $\frac{25^\circ}{25^\circ}$ = ·8008 (P.). Sp. heat = ·686; of a mixture of 1 mol. $C_4H_{10}O$ + 50 mols. H_2O = 1·086, 1 mol. $C_4H_{10}O + 70\ H_2O$ = 1·067 (Pagliani, N. Cim. [3] 12, 229 [1883]). H.F.p. = 71,150; H.F.v. = 68,540 (Thomsen, Th. 4, 162). M.M. = 4·936 at 17·7° (P.); $R_\infty = 35·41$; μ_β = 1·4007. Capillarity constant at b.p. $\alpha^2 = 4·416$ (Schiff, A. 223, 70). Vap. pressure:

At 14·75° =	5·8 mm.	At 70·7° =	160·1 mm.
„ 30·85° =	17·7 „	„ 80·0° =	246·0 „
„ 50·45° =	55·5 „	„ 91·0° =	395·2 „
„ 60·4° =	94·1 „	„ 99·9° =	570·3 „

(Konovalow, P. [2] 14, 42) (*v.* also Naccari a. Pagliani, J. 1882, 63). Sp.gr. of aqueous solutions (Duclaux, A. Ch. [5] 13, 91):

Percentage of alcohol (by vol.)	2·5	5	6	10
Sp.gr. of aqueous solution at 15°	·9950,	·9930,	·9915,	·9875

Occurs in fusel oil from potatoes and beet (Wurtz, A. Ch. [3] 42, 129), and combined with angelic and isobutyric acids in Roman oil of chamomile (Köbig, A. 195, 96).

Preparation.—By the action of sodium-amalgam and water upon β-chlor-isobutyl alcohol, which results from the action of hypochlorous acid upon isobutylene (Butlerow, A. 144, 24). Is formed in small quantity by the action of elliptical yeast upon sugar or glycerin (Claudon a. Morin, C. J. 52, 714).

Properties.—Colourless liquid, soluble in 10·5 parts of water, from which calcium chloride causes it to separate. Smells like fusel oil. Is oxidised by chromic acid into isobutyric acid, acetic acid, carbon dioxide, acetone, and other products (Krämer, B. 7, 252). Zinc-dust yields water and isobutylene (Jahn, B. 13, 989). For combinations and derivatives *v.* Gladstone a. Tribe, C. J. 39, 6; Pierre a. Puchot, A. 163, 274, and Heindl, M. 2, 208.

3. *Secondary tetryl alcohol.* Methyl ethyl carbinol, butylene hydrate, $\begin{matrix}C_2H_5\\CH_3\end{matrix}>CHOH$; b.p. 99° at 738·8 mm. (Lieben, A. 150, 114); sp.gr. $\frac{0^\circ}{\;}$ = ·827, $\frac{22}{\;}$ = ·810 (L.).

Formed by the action of water upon the compound of zinc-ethyl and aldehyde:

$$CH_3CH(C_2H_5)O.Zn(C_2H_5).$$

thus

$$CH_3CH(C_2H_5)O.ZnC_2H_5 + H_2O = C_4H_9OH + ZnO + C_2H_6$$

(Wagner, A. 181, 261). Also by acting upon secondary tetryl iodide with silver acetate and saponifying the resulting acetate by means of potash (Luynes, A. 125, 252; 128, 330; 128, 274). Normal tetryl alcohol may be changed into the secondary alcohol; the normal iodide is heated with potash, and the normal butylene so obtained on treatment with hydriodic acid yields secondary tetryl iodide (Saytzen, Z. 1870, 327).

Properties.—Liquid, with strong odour; upon oxidation yields a ketone $C_2H_5.CO.CH_3$ (b.p. = 80°), and acetic acid (Saytzen). Heated with a trace of hydrochloric, hydrobromic, or hydriodic acid, in a sealed tube, to 240°, yields C_4H_8 (pseudo-butylene).

4. *Tertiary tetryl alcohol.* Trimethyl carbinol $(CH_3)_3C.OH$. A solid; m.p. 25°; b.p. 82·94° (cor.) (Linnemann, A. 162, 26); 81·5–82° (Perkin, C. J. 45, 421). Sp.gr. $\frac{37^\circ}{}$ = ·7792 (L.); $\frac{30^\circ}{}$ = ·7788 (Butlerow, A. 162, 229); $\frac{20^\circ}{4^\circ}$ = ·7864; $\frac{26^\circ}{4^\circ}$ = ·7802 (Brühl, A. 203, 17); $\frac{25^\circ}{25^\circ}$ = ·7836; $\frac{35^\circ}{35^\circ}$ = ·7761 (P.); M.M. at 24·3° = 5·122 (P.); μ_β = 1·3924; R_∞ = 35·53; H.C. (solid) = 632818 cal. (Luginin, A. Ch. [5] 25, 142); H.C. (vapour) = 643,500 (Thomsen, Th. 4, 163); H.F.p. = 88,300; H.F.v. = 85,690 (T.); crit. temp. = 234·9° (Pawlewski, B. 16, 2634).

Formed from isobutyl iodide by treatment with acetic acid and silver oxide (Linnemann; Butlerow, A. 168, 143); also from isobutylamine by treatment with nitrous acid and from isobutyl carbimide $CO.N.C_4H_9$, by action of potash (Linnemann, A. 162, 12). Can be prepared by allowing 20 grms. of tertiary tetryl iodide and 50 grms. of water to stand in contact for two or three days (Dobbin, C. J. 37, 238).

Isobutyl alcohol heated with excess of hydrochloric acid yields a mixture of secondary and tertiary tetryl chlorides, and when heated with six volumes of water only the latter is decomposed, yielding the alcohol and hydrochloric acid (Freund, J. pr. [2] 12, 25).

Properties.—Forms rhombic plates or prisms. Unites with water to form a liquid hydrate $2C_4H_{10}O.H_2O$ (b.p. 80°, sp.gr. $\frac{0^\circ}{}$ = ·8276) (Butlerow, A. 162, 229). On oxidation yields acetone, carbon dioxide, acetic acid, and a small quantity of isobutyric acid (Butlerow, Z. 1871, 485). In sunlight it combines with chlorine, forming tertiary tetryl chloride and other bodies (D'Otreppe, J. 1881, 512).

Tertiary butyl alcohol has a slightly narcotic action when taken internally, and is found in the urine in combination with glycuronic acid (Thierfelder a. v. Mering, H. 9, 511).

Tetryl bromides. Butyl bromides C_4H_9Br.

1. *Normal tetryl bromide*

$CH_3.CH_2.CH_2.CH_2Br$;

b.p. 100·4° at 744 mm. (Lieben a. Rossi, A. 158, 161); 99·9° (cor.) (Linnemann, A. 161, 193). Sp.gr. $\frac{0^\circ}{}$ = 1·3050; $\frac{20^\circ}{}$ = 1·2792; $\frac{40^\circ}{}$ = 1·2571 (L. a. R.); $\frac{0^\circ}{}$ = 1·305; $\frac{20^\circ}{}$ = 1·299 (L.).

Formed from normal tetryl alcohol and hydrobromic acid (L. a. R.).

By the action of bromine, dibromtetrane $C_4H_8Br_2$ (b.p. 166°) is formed (L.).

2. *Isotetryl bromide* $(CH_3)_2CH.CH_2Br$; b.p. 92·3° (cor.) (Linnemann, A. 162, 34); 91·3° (Perkin, C. J. 45, 459); sp.gr. $\frac{16^\circ}{}$ = 1·2038 (L.), $\frac{15^\circ}{15^\circ}$ = 1·2722; $\frac{25^\circ}{25^\circ}$ = 1·2598 (P.). Capillarity constant at b.p. a^2 = 3·103; M.V. = 118·39 (Schiff, G. 14, 368); M.M. = 8·003 at 16·2° (P.). From isobutyl alcohol, bromine, and phosphorus (Wurtz, A. 93, 114). Unites with bromine at 150° to form $C_4H_7Br_3$ (L.).

3. *Tertiary tetryl bromide* $(CH_3)_3CBr$; b.p. 72° at 761·5 mm.; 70·5–72·5° (Perkin); sp.gr. $\frac{20^\circ}{}$ = 1·215; $\frac{15^\circ}{15^\circ}$ = 1·2020; $\frac{25^\circ}{25^\circ}$ = 1·1892; M.M. = 8·238 at 17·8° (P.). Formed when isobutyl bromide is heated to 240° (Eltekow, B. 8, 1244). Also from trimethyl carbinol and phosphorous bromide (Reboul, J. 1881, 409). May also be prepared by leading isobutylene into a solution of hydrobromic acid of sp.gr. 1·7 (Roozeboom, B. 14, 2396). Is readily decomposed at 300° into isobutylene and hydrobromic acid. Water, in the cold, forms the alcohol.

Tetryl chlorides. Butyl chlorides C_4H_9Cl.

1. *Normal tetryl chloride*

$CH_3.CH_2.CH_2.CH_2Cl$;

b.p. = 77·6° at 741·3 mm. (Lieben a. Rossi, A. 158, 161); 77·96° (cor.) (Linnemann, A. 161, 197); sp.gr. $\frac{0^\circ}{}$ = ·9074; $\frac{20^\circ}{}$ = ·8874 (L. a. R.); $\frac{0^\circ}{}$ = ·9074 (L.); $\frac{14^\circ}{}$ = ·8974. Formed by the action of chlorine upon *n*-tetrane (Pelouze a. Cahours, J. 1863, 524). More easily by the action of hydrochloric acid upon *n*-tetryl alcohol (Lieben a. Rossi).

2. *Isotetryl chloride* $(CH_3)_2CH.CH_2Cl$; b.p. = 68·5° (Linnemann, A. 162, 17); 68·5–69° (Perkin, C. J. 45, 421). Sp.gr. $\frac{15^\circ}{}$ = ·8798 (L.); $\frac{0^\circ}{}$ = ·8953; $\frac{27{\cdot}8^\circ}{}$ = ·8651; $\frac{59^\circ}{}$ = ·8281 (Pierre, Puchot, A. 163, 276); $\frac{15^\circ}{15^\circ}$ = ·8835; $\frac{25^\circ}{25^\circ}$ = ·8739 (P.). M.M. at 21·3° = 6·144 (Perkin). Capillarity const. at b.p. a^2 = 4·127; M.V. = 114·26 (Schiff, G. 14, 368); H.F.v. = 43,050 (Thomsen, Th. 4, 281). Formed by the action of hydrochloric acid or of PCl_5 upon the alcohol (Wurtz, A. 93, 113). By the action of chlorine $C_4H_4Cl_6$ is produced.

3. *Tertiary tetryl chloride* $(CH_3)_3CCl$; b.p. = 50–51° (Butlerow, J. 1864, 497; A. 144, 33), 51–52° (Perkin, C. J. 45, 421). Sp.gr. $\frac{0^\circ}{}$ = ·8658 (Puchot), $\frac{15^\circ}{15^\circ}$ = ·8471; $\frac{25^\circ}{25^\circ}$ = ·8368; M.M. at 15° = ·6·257 (Perkin).

Formed (1) by the chlorination of tertiary tetrane (Butlerow); (2) by the action of iodine monochloride upon isotetryl iodide (Linnemann, A. 162, 18); (3) by the action of hydrochloric acid upon isobutylene at 100° (Zalessky, B. 5, 480; Le Bel, Bl. 28, 462); (4) by the action of phosphorus pentachloride upon the alcohol.

Heated with five or six vols. of water to 100° the alcohol is produced (Butlerow, A. 144, 33). Chlorine in diffused daylight forms $C_4H_8Cl_2$ (b.p. 106–107°), $C_4H_7Cl_3$ and $C_4H_5Cl_5$, whilst in direct sunlight $C_4H_4Cl_6$ (b.p. in partial vacuum about 115°), and other products are formed (D'Ottreppe, J. 1882, 461).

Tetryl cyanates. Only the iso-cyanates have been described.

1. *Isotetryl isocyanate*

$(CH_3)_2CH.CH_2.N.CO.$

Isobutyl carbimide; b.p. 110° by the distillation of isotetryl iodide with silver cyanate and sand (Brauner, B. 12, 1877).

2. *Tertiary tetryl isocyanate*

$(CH_3)_3C.NCO$;

b.p. 85·5° (cor.). Sp.gr. $\frac{0^\circ}{}$ = ·8676; remains liquid at −25°. Is formed, together with other bodies, when silver cyanate acts upon isotetryl iodide (Brauner, B. 12, 1874). By the action of potash or of hydrochloric acid we get tertiary tetrylamine $(CH_3)_3C.NH_2$.

Tetryl cyanides. Valeronitriles C_4H_9CN.

1. *Normal tetryl cyanide*

$CH_3.CH_2.CH_2.CH_2CN$;

b.p. 140·4° at 739·3 mm. Sp.gr. $\frac{0^\circ}{}$ = ·8164 (Lieben a. Rossi, A. 158, 171).

2. *Isotetryl cyanide* $(CH_3)_2.CH.CH_2.CN$; b.p. 126–128° at 714 mm. (Erlenmeyer a. Hell, A. 160, 266), 129·3–129·5° at 764·3° (R. Schiff, B. 19, 567). Sp.gr. $\frac{0^\circ}{}$ = ·8227, $\frac{20^\circ}{}$ = ·8069 (E. a. H.), $\frac{129^\circ}{4^\circ}$ = ·6921 (S.). Formed by the oxidation of gelatine (Schlieper, A. 59, 15) or caseine (Gunckelberger, A. 64, 76) with chromic acid; also by the action of P_2O_5 upon ammonium isovalerate (Dumas, Malaguti, a. Leblanc, A. 64, 334). May be prepared by heating 300 grms. isobutyl-iodide, 98 grms. of potassium cyanide, 98 grms. of alcohol, and 25 grms. of water for three days on the water-bath (E. a. H.).

3. *Tertiary tetryl cyanide* $(CH_3).C.CN$; m.p. 15–16°; b.p. 105–106°. Formed by mixing 100 parts of tertiary tetryl iodide, 110 parts of mercury potassium cyanide $Hg(CN)_2.2KCN$ with 75 parts of dry magnesia, and allowing the mixture to remain for two or three days at a temperature not exceeding 5°. The mass is then treated with water, and distilled on the paraffin-bath (Butlerow, A. 170, 154).

Tetryl hydrides. Tetranes, butanes.

1. *Normal tetrane*, *n*-butane, diethyl, methyl propane $CH_3.CH_2.CH_2.CH_3$; b.p. 1° (Butlerow, Z. 1867, 363). Sp.gr. $\frac{0^\circ}{}$ = ·60 (Ronalds, C. J. 18, 54). V.D. = 2·046. Occurs in crude petroleum (Ronalds, Lefebvre, Z. 1869, 185). Formed by heating ethyl iodide with zinc to 150° (Frankland, A. 71, 173; Schöyen, A. 130, 233). Also by the action of sodium-amalgam upon ethyl iodide (Löwig, J. 1860, 397). A colourless gas, insoluble in water. 1 vol. of alcohol at 14·2° and 744·8 mm. absorbs 18·13 vols. of butane (Frankland).

2. *Isotetrane.* Isobutane, trimethylmethane $(CH_3)_3CH$; b.p. = −17°. H.F.p. = 42,450. H.F.v. = 40,130 (Thomsen, Th. 4, 54). Formed by heating ·9 part of isobutyl iodide with 2·4 parts of aluminium chloride to 120° (Köhnlein, B. 16, 562). Also by the action of zinc and water upon tertiary butyl iodide (Butlerow, A. 144, 10). The gas is readily soluble in alcohol, from which it can be expelled by dilution with water.

Tetryl iodides. Butyl iodides C_4H_9I.

1. *Normal tetryl iodide*

$CH_3.CH_2.CH_2.CH_2I$;

b.p. 129·6° at 738·2° mm. (Lieben a. Rossi, A. 158, 163); 129·8° (cor.) (Linnemann, A. 161, 196); 130·4–131·4° at 745·4 mm. (Brühl, A. 203, 21). Sp.gr. $\frac{0^\circ}{}$ = 1·643, $\frac{20^\circ}{}$ = 1·6136 (L. a. R.), $\frac{20^\circ}{4^\circ}$ = 1·6166 (Brühl). From *n*-tetryl alcohol and hydriodic acid (Linnemann, A. 161, 196). By the action of iodine trichloride at 250° it yields perchlorethane C_2Cl_6 (Krafft, B. 10, 805).

2. *Isotetryl iodide* $(CH_3)_2.CH.CH_2I$; b.p. 120·0° (cor.) (Linnemann, A. 160, 240; 192, 69), 119·4–120·4° at 745·4 mm. (Brühl, A. 203, 21), 83–83·25° at 250 mm. (Perkin, C. J. 45, 421). Sp.gr. $\frac{0^\circ}{}$ = 1·6401 (L.), $\frac{20^\circ}{4^\circ}$ = 1·6056 (Brühl), $\frac{15^\circ}{15^\circ}$ = 1·6138, $\frac{25^\circ}{25^\circ}$ = 1·6007 (P.). M.M. at 19·4° = 12·199 (P.). Capillarity const. a^2 = 2·533; S.V. = 128·25 (Schiff, G. 14, 368). From isobutyl alcohol, phosphorus, and iodine (Wurtz, A. 93, 116).

3. *Secondary tetryl iodide*

$C_2H_5.CHI.CH_3$;

b.p. 117–118° (Luynes, Bl. 2, 3), 119–120° (Lieben, A. 150, 96). Sp.gr. $\frac{0^\circ}{0^\circ}$ = 1·6263, $\frac{20^\circ}{0^\circ}$ = 1·5952, $\frac{30^\circ}{0^\circ}$ = 1·5787 (Lieben), $\frac{0^\circ}{}$ = 1·632, $\frac{20^\circ}{}$ = 1·604 (Luynes). Formed by distilling erythrite with hydriodic acid (Luynes) or from *n*-butylene and hydriodic acid (Wurtz, A. 152, 23).

4. *Tertiary tetryl iodide* $(CH_3)_3CI$; b.p. (with decom.) = 98–99° (Butlerow); 100·3° (Puchot, A. Ch. [5] 28, 546). Sp.gr. $\frac{0^\circ}{}$ = 1·571, $\frac{53^\circ}{}$ = 1·479 (P.). From tertiary tetryl alcohol and hydriodic acid or isobutylene and hydriodic acid (Butlerow, A. 144, 5, 122); is easily decomposed (by silver oxide, potash, or by heating with zinc and water), into hydriodic acid and isotetrylene (Butlerow, Z. 1867, 362). Is also decomposed by water in the cold yielding hydriodic acid and tertiary tetryl alcohol. On heating with sodium yields a mixture of hydrogen, isotetrylene, and isotritetrylene $(C_{12}H_{24})$ (Dobbin, C. J. 37, 236).

Tetryl mercaptans $C_4H_9.SH$.

1. *Normal tetryl mercaptan*

$CH_3.CH_2.CH_2.CH_2.SH$

b.p. 97–98°: sp.gr. $\frac{0^\circ}{}$ = ·858 (Saytzen a. Grabowsky, A. 171, 251; 175, 351).

2. *Isotetryl mercaptan*

$(CH_3)_2CH.CH_2SH$;

b.p. 88°; sp.gr. $\frac{11{\cdot}5^\circ}{}$ = ·848 (Humann, A. 95, 256), $\frac{20^\circ}{4^\circ}$ = ·83573 (Nasini, B. 15, 2882).

3. *Secondary tetryl mercaptan*

$(CH_3)_3CH.SH$;

b.p. 84–85°; sp.gr. $\frac{17^\circ}{}$ = ·8299. The mercury compound $(C_4H_9S)_2Hg$ melts at 189° (Reymann, B. 7, 1287).

Tetryl nitrate.

Isotetryl nitrate $CH_3.CH_2.CH_2.CH_2.NO_3$; b.p. 123°; sp.gr. $\frac{0^\circ}{}$ = 1·0384, M.M. at 8·9° = 5·18 (P.); mol. refraction = 46·72 (P.); b.p. 123·5–124·5° (Perkin, C. J. 55, 684); $\frac{4^\circ}{4^\circ}$ = 1·0334, $\frac{10^\circ}{10^\circ}$ = 1·0264, $\frac{25^\circ}{25^\circ}$ = 1·0124 (P.). From silver nitrate, urea, and isobutyl iodide (Wurtz, A. 93 120; Chapman a. Smith, Z. 1869, 433).

Tetryl nitrites $C_4H_9NO_2$.

1. *Isotetryl nitrite* $(CH_3)_2CHCH_2NO_2$; b.p. 67° (Chapman a. Smith, Z. 1869, 433), 67·3–67·5° (cor.) at 755 mm. (Thomsen, Th. 4, 217). Sp.gr. $\frac{0^\circ}{} = \cdot 89445$ (C. a. S.); $\frac{4^\circ}{4^\circ} = \cdot 8878$, $\frac{10^\circ}{10^\circ} = \cdot 8806$, $\frac{15^\circ}{15^\circ} = \cdot 8752$, $\frac{20^\circ}{20^\circ} = \cdot 8702$, $\frac{25^\circ}{25^\circ} = \cdot 8652$. M.M. at 8·2° = 5·51; mol. refraction = 43·9 (Perkin, C. J. 55, 686 and 757); H.F.p. = 47,800; H.F.v. = 44,900 (Thomsen, Th. 4, 218). Sp.gr. $\frac{15^\circ}{15^\circ} = \cdot 876$, b.p. 67°. Prepared by mixing isobutyl alcohol and sulphuric acid. On cooling, the mixture is poured gradually into an aqueous solution of sodium nitrite (1:3); the upper layer, consisting of isotetryl nitrite, is decanted, washed with potassium carbonate solution, and dried. It is a pale-yellow liquid, is apt to become acid by keeping, and then rapid decomposition sets in. Taken medicinally, lowers the blood pressure and produces respiratory paralysis (Dunstan a. Wooley, Ph. [3] 19, 487).

2. *Tertiary tetryl nitrite* $(CH_3).CH.NO_2$; b.p. 63°; sp.gr. $\frac{0^\circ}{} = \cdot 8914$ (Bertoni, G. 15, 351), 67–68° (Tscherniak, A. 180, 155). From the alcohol and glyceryl nitrite (B.); also from the iodide and silver nitrite (T.). A yellow, mobile liquid; soluble in alcohol, ether, and chloroform; sparingly soluble in water.

Tetryl oxides $(C_4H_9)_2O$.

1. *Normal tetryl oxide*; b.p. 140·5° at 741·5 mm. (Lieben a. Rossi, A. 165, 110); 141° (Reboul, C. R. 108, 39). Sp.gr. $\frac{0^\circ}{} = \cdot 784$, $\frac{20^\circ}{} = \cdot 7685$ (L. a. R.). By the action of the sodium derivatives of the alcohol upon *n*-butyl bromide (R.).

2. *Isotetryl oxide* $[(CH_3)_2CH.CH_2]_2O$; b.p. 100–104° (Wurtz, A. Ch. [3] 42, 153); 122–122·5° (Reboul, C. R. 108, 162). Sp.gr. $\frac{15^\circ}{} = \cdot 7616$ (R.). From isotetryl iodide and sodium isotetrylate (R.). The action of isotetryl iodide upon potassium isotetrylate—which, according to Wurtz, yields this oxide—really gives a mixture of isoditetrylene and isotetryl alcohol (Reboul).

3. *Secondary tetryl oxide*
$[C_2H_5CH(CH_3)]_2O$;
b.p. 120–121°; sp.gr. $\frac{21^\circ}{} = \cdot 756$ (Kessel, A. 175, 50). From ethylidene chlorhydrin, and zinc-ethyl (K.). Found in mere traces only by the action of sec-tetryl bromide upon the sodium derivative of the secondary alcohol (Reboul, C. R. 108, 162). Reboul obtained also the following mixed ethers:—

Secondary tetryl isotetryl ether; b.p. 121–122°; sp.gr. $\frac{15^\circ}{} = \cdot 7652$;

Tertiary tetryl isotetryl ether;

Normal tetryl isotetryl ether; b.p. 131·5°; sp.gr. $\frac{15\cdot 5^\circ}{} = \cdot 763$;

Normal tetryl secondary tetryl ether; b.p. 131°; sp.gr. $\frac{15^\circ}{} = \cdot 7687$;

Normal tetryl tertiary tetryl ether; b.p. 124°; but could not obtain the secondary tertiary and the di-tertiary ethers.

Tetryl sulphides.

1. *Normal tetryl sulphide*
$[CH_3(CH_2)_3]_2S$;
b.p. 182°; sp.gr. $\frac{0^\circ}{} = \cdot 8523$ (Saytzen, A. 171, 253). From tetryl iodide and potassium sulphide. Nitric acid yields the sulphone $(C_4H_9)_2SO_2$ (m.p. 43·5°) (Grabowsky, A. 175, 348).

2. *Isotetryl sulphide* $[(CH_3)_2CH.CH_2]_2S$; b.p. 172–173° at 747 mm. (Grabowsky a. Saytzen, A. 171, 254), 170·5° at 752 mm. (Beckmann, J. pr. [2] 17, 445); sp.gr. $\frac{10^\circ}{} = \cdot 8363$ (B.).

Isotetryl disulphide $(C_4H_9)_2S_2$; b.p. 220° (Spring a. Legros, B. 15, 1940).

3. *Secondary tetryl sulphide*
$(CH_3.CH.C_2H_5)_2S$;
b.p. 165°; sp.gr. $\frac{23^\circ}{} = \cdot 8317$ (Reymann, B. 7, 1288).

Tetryl thiocarbimides. Butyl mustard oils; isothiocyanates.

1. *Normal tetryl thiocarbimide*
$(C_4H_9)NCS$;
b.p. 167° (Hofmann, B. 7, 512). From tetryl amine, carbon disulphide, and alcohol (H.).

2. *Isotetryl thiocarbimide*
$(CH_3)_2CH.CH_2.NCS$;
b.p. 162°; sp.gr. $\frac{14^\circ}{} = \cdot 9638$ (Hofmann, B. 7, 511).

3. *Secondary tetryl thiocarbimide*
$C_2H_5.CH(CH_3)NCS$;
b.p. 159·5°; sp.gr. $\frac{12^\circ}{} = \cdot 944$. Occurs in the ethereal oil from spoon wort (*Cochlearia officinalis* (Hofmann, B. 2, 102; 7, 512).

4. *Tertiary tetryl thiocarbimide*
$(CH_3)_3C.NCS$;
m.p. 10·5°; b.p. = 140° at 770·3 mm.; sp.gr. $\frac{10^\circ}{} = \cdot 9187$, $\frac{34^\circ}{} = \cdot 9003$ (Rudnew, J. R. 11, 179). Has a pleasant aromatic odour.

TETRYLAMINES.

1. Monotetrylamines.

(*a*) *Normal tetrylamine*
$CH_3.CH_2.CH_2.CH_2.NH_2$;
b.p. 75·5° at 740 mm. (Lieben a. Rossi, A. 158, 172); sp.gr. $\frac{0^\circ}{} = \cdot 7553$, $\frac{26^\circ}{} = \cdot 7333$ (L. and R.), $\frac{20^\circ}{} = \cdot 7401$ (Linnemann a. Zotta, A. 162, 3). Formed by the action of caustic potash upon tetryl cyanate (Lieben a. Rossi); also from propyl cyanide by zinc and sulphuric acid (Linnermann a. Zotta), or from nitrotetrane by action of tin and hydrochloric acid (Züblin, B. 10, 2083). Is miscible with water; reduces copper, silver, and mercury solutions in presence of alkalis. The chloride forms a yellow crystalline compound with $PtCl_4$, which is almost insoluble in cold water.

(*b*) *Iso-tetrylamine* $(CH_3)_2CH.CH_2.NH_2$; b.p. 68° (Schiff, B. 19, 565), 65·5° (Hughes a. Römer, B. 7, 511), 68–69° (Perkin, C. J. 55, 694); sp.gr. $\frac{15^\circ}{} = \cdot 7357$ (Linnemann, A. 162, 23), $\frac{4^\circ}{4^\circ} = \cdot 7464$, $\frac{10^\circ}{10^\circ} = \cdot 7408$, $\frac{15^\circ}{15^\circ} = \cdot 7363$, $\frac{25^\circ}{25^\circ} = \cdot 7283$; M.M. at 15·3° = 5·692 (P.). H.F.p. = 38,460. H.F.v. = 35,560. H.C. = 726,990 (Thomsen, Th. 4, 140). From isotetryl cyanate and potash (Linnemann, A. 162, 23); also from isotetryl iodide and ammonia (Hughes a. Römer); also from isotetryl chloride and ammonia dissolved in water or isotetryl alcohol. All three isotetrylamines are produced, the tri-isotetrylamine in largest quantity. The bases can then be separated by means of ethyl oxalate. The product is first separated into two fractions, the one rich in the mono-isotetrylamine, the other rich in the di- and tri- compounds. To the former water and then ethyl oxalate are added; the primary base is thus converted into the oxamide $C_2O_2(NHC_4H_9)_2$, which is almost insoluble in boiling water, the secondary amine being changed into ethyl oxamate $C_2H_5O.C_2O_2.N(C_4H_9)_2$. The other fraction (anhydrous) being poured into ethyl oxalate, the primary and secondary bases are converted into oxamates. The tertiary base is distilled off, and the oxamates are saponified by heating with slaked lime. The calcium oxamates can be separated by crystallisation, the diisotetryloxamate being the more soluble in alcohol, from which it separates in slender silky needles (Malbot, C. R. 104, 228).

Can be produced by heating isotetryl alcohol with ammoniacal zinc chloride to 260° (Merz a. Gasiorowski, B. 17, 624), or by the action of caustic potash (10 p.c. solution) upon a mixture of bromine and isovaleramide (equal molecules) at 60° (Hofmann, B. 15, 769).

Mixed with water contraction and development of heat are produced. A mixture of equal volumes of water and isotetrylamine has a sp.gr. $\frac{15^\circ}{15^\circ}$ of ·9002, instead of the average density ·8681 (Perkin, C. J. 55, 695). With absolute alcohol and the amine similar results were obtained, the sp.gr. of a mixture of equal volumes being $\frac{15}{15^\circ}$ = ·791, instead of ·7652, the calculated number.

(*c*) *Secondary tetrylamine*

$C_2H_5.CHNH_2.CH_3$;

b.p. 63°. Formed by the action of potash upon secondary tetryl cyanate, or of ammonia upon secondary tetryl iodide (Hofmann, B. 7, 513). Also by the action of dilute sulphuric acid upon secondary tetryl mustard oil (Reymann, B. 7, 1289).

(*d*) *Tertiary tetrylamine* $(CH_3)_3C.NH_2)$; b.p. 45·2° at 760 mm. (Rudnew, R. 11, 163); sp.gr. $\frac{0^\circ}{}$ = ·7137; $\frac{8^\circ}{}$ = ·7054; $\frac{15^\circ}{}$ = ·6931 (R.). Formed in small quantity by the action of potash upon isotetryl cyanate (Linnemann, A. 162, 19; Hofmann, B. 7, 513). Also as a by-product in preparing tri-methyl acetic acid from trimethyl carbinol iodide and mercuric cyanide (Rudnew).

2. **Ditetryl-amines.**

(*a*) *Di-normal tetryl amine*

$(CH_3.CH_2.CH_2.CH_2)_2NH$;

b.p. 160°. Formed in small quantities by the action of potash upon butyl cyanate (Lieben a. Rossi, A. 158, 175) $[(C_4H_9)_2NH.HCl]_2PtCl_4$; long yellow needles, almost insoluble in cold water.

(*b*) *Di-iso-tetrylamine*

$[(C.H_3)_2CH.CH_2]_2NH$;

b.p. 135–137°. From isotetryl bromide and alcoholic ammonia at 150° (Ladenburg, B. 12, 949); also from isotetryl alcohol and ammoniacal zinc chloride at 270° (Merz a. Gasiorowski, B. 17, 627). The hydrochlorate $(C_4H_9)_2NH.HCl$ forms plates or leaflets easily soluble in alcohol and water, slightly in ether. The platinum compound forms dark-red prisms, soluble in water, alcohol, and ether (Malbot, C. R. 104, 366). The nitroso- derivative $(C_4H_9)_2N.NO$ is a disagreeably smelling oil; m.p. 0°; b.p. 213–216° (with decomposition) obtained by the action of potassium nitrite upon the hydrochlorate (Ladenburg, B. 12, 949).

(*c*) *Di-tertiary tetrylamine*

$[(CH_3)_3C]_2NH$;

produced as iodide when tertiary tetryl iodide and tertiary tetrylamine are heated to 50°, at 70° the mixture is decomposed, forming isotetrylene and tertiary tetrylamine hydroiodide (Rudnew, J. R. 11, 174). The hydroiodide is easily soluble in water or alcohol on heating; the aqueous solution evolves tertiary tetrylamine.

3. **Tri-tetrylamines.**

(*a*) *Tri-normal tetrylamine* $(C_4H_9)_3N$; b.p. 211–215° at 740 mm.; sp.gr. $\frac{0}{}$ = ·791, $\frac{20}{}$ = ·7782, $\frac{40}{}$ = ·7677. From tetryl cyanate and potash, together with the mono- and di- compounds (Lieben a. Rossi, A. 165, 115). With tetryl iodide forms iodide of tetratetrylammonium $N(C_4H_9)_4I$, which crystallises in small plates (L. a. R.).

(*b*) *Tri-iso-tetrylamine* $(C_4H_9)_3N$; b.p. 177–180° (Reimer, B. 3, 757); 184–186° (Sachtleben, B. 11, 733). Sp.gr. $\frac{21^\circ}{}$ = ·785 (S.). From di-iso-tetrylamine and isotetryl bromide (R.). From the alcohol and ammoniacal zinc chloride at 270° (Merz a. Gasiorowski, B. 17, 627); also from isotetryl iodide and aqueous ammonia at 160° (Malbot, C. R. 105, 574). Is not miscible with water. Forms salts with hydrochloric, nitric, and sulphuric acids, which are extremely soluble and crystallise with difficulty. The platinum double salt forms large ruby red crystals (Malbot, C. R. 104, 366).

Tetrylene C_4H_8. Three isomeric bodies are possible and are known.

1. *Normal* (α)*-tetrylene.* Butylene, ethyl ethylene, $CH_3.CH_2.CH:CH_2$; b.p. −5°.

Formation.—From normal tetryl iodide and alcoholic potash (Saytzen, J. pr. [2] 3, 88; Grabowsky a. Saytzen, A. 179, 330). From bromethylene and zinc-ethyl (Wurtz, A. 152, 21). From normal tetrylamine and nitrous acid (v. Meyer, B. 10, 136). Prepared by digesting on the water-bath 100 grms. normal tetryl iodide, 200 grms. potash, and 150 grms. of alcohol (90 p.c.) (S.). A gas at ordinary temperatures, which combines readily with hydriodic acid to form secondary tetryl iodide, and with hypochlorous acid, forming chloro-methyl-ethyl carbinol

$CH_3.CH_2.CH(OH).CH_2Cl$;

2. *β-tetrylene.* Pseudotetrylene; symmetrical dimethylethylene $CH_3.CH:CH.CH_3$; b.p. 1° at 741·4 mm. (Lieben, A. 150, 108); $\frac{-13·5^\circ}{}$ = ·635 (Puchot, Bl. 30, 188).

Formed by the action of potash upon secondary tetryl iodide (Luynes, A. 129, 200; Lieben, A. 150, 108). Together with isotetrylene by dropping iso- or normal tetryl alcohol upon strongly-heated zinc chloride (Nevole, Bl. 24, 122; Le Bel a. Greene, Am. 2, 23). From trithioaldehyde $(C_2H_4S)_3$ and copper (Eltekow, B. 10, 1904). By heating a mixture of methyl iodide and allyl iodide with sodium (Wurtz, A. 144, 235).

Preparation.—Isotetryl alcohol is allowed to drop upon heated zinc chloride and the evolved gas is led into sulphuric acid diluted with half its volume of water; this retains the isotetrylene. The unabsorbed gas is led into bromine, and is again liberated by action of sodium (Le Bel a. Greene, Bl. 29, 306).

β-tetrylene combines with bromine to form a dibromide boiling at 156–158°. This body, by the action of potash, forms mono-bromo-pseudo-tetrylene $CH_3CBr{:}CH.CH_3$; b.p. 87–88° (Hölz, A. 250, 230). Chlorine forms a di-chloride, b.p. 112–114° (Chechoukow, Bl. 43, 127).

3. *γ-tetrylene.* Iso-tetrylene, unsymmetrical dimethyl ethylene $(CH_3)_2C{:}CH_2$; b.p. −6° (Butlerow, Z. 1870, 236); absolute b.p. = 150·7° (Nadeschin, B. 15 [2] 27); H.F.p. = 10,660. H.F.v. = 8,920; H.C. = 650,620 (Thomsen, Th. 4, 70). Liquefied by a pressure of 2–2½ atmospheres at 15–18°. Is produced by the dry distillation of fats (Faraday, Tr. 1825, 440); by heating the vapour of fusel oil to redness (Wurtz, A. 104, 249), together with ethylene and ethane; also from light petroleum, 'ligroin' (b.p. 60–90°) (Prunier, J. 1873, 347); from iso- or tertiary-tetryl iodide and alcoholic potash (Butlerow, A. 144, 19); by heating trimethyl carbinol and dilute sulphuric acid (1 vol. H_2SO_4 to 2 vols. water) (Butlerow); from iso-tetryl alcohol and zinc chloride, though in very small quantity (Nevole, Bl. 24, 122).

Preparation.—5 parts of isotetryl alcohol, 5 parts sulphuric acid, 1 part of water and sand are heated together (Lermontow, A. 196, 117). Puchot's method (A. Ch. [5] 28, 508) of heating isotetryl alcohol with a mixture of sulphuric acid, potassium sulphate, and gypsum gives a mixture of pseudo and iso-tetrylene (Scheschukow, J. R. 16, 510). A mixture of 2 parts of caustic potash and 3 parts of alcohol (90 p.c.) is little by little added to 2 parts of iso-tetryl iodide and gently warmed (Butlerow, Z. 1870, 238). A gas, with unpleasant smell, slightly soluble in water, combines with hydriodic acid to form tertiary tetryl iodide (*v.* Scheschukow, J. R. 1886, 207). A mixture of three parts of sulphuric acid and 1 part of water completely absorbs the gas, which on dilution and distillation comes off as trimethyl carbinol. Oxidising agents—*e.g.* potassium permanganate—form carbon dioxide, formic and acetic acids, and oxalic acid (and in the case of chromium trioxide, acetone) (Zeidler, A. 197, 251). By the action of a mixture of 5 parts sulphuric acid and 1 part of water forms dodecylene $C_{12}H_{24}$, b.p. 177·5–178·5°; sp.gr. $\frac{0^\circ}{} = {\cdot}774$ (Butlerow, B. 6, 561).

Tetrylene alcohol *v. Tetrylene glycols.*

Tetrylene bromides.

1. *Normal tetrylene bromide*

$CH_3.CH_2.CHBr.CH_2Br.$;

b.p. 165·6–166°; sp.gr. $\frac{0^\circ}{} = 1{\cdot}876$ (Wurtz, A. 152, 23), $\frac{0^\circ}{} = 1{\cdot}8503$, $\frac{20^\circ}{0^\circ} = 1{\cdot}8204$ (Grabowsky a. Saytzen, A. 179, 332). Formed from α-tetrylene and bromine (Wurtz). From normal tetryl bromide and bromine at 150° (Linnemann, A. 161, 199). Gives α-tetrylene by action of sodium.

2. *β-Tetrylene bromine*

$CH_3CHBr.CHBr.CH_3$;

b.p. 158°; sp.gr. $\frac{0^\circ}{}$ 1·821. Formed from β-tetrylene and bromine (Wurtz, A. 144, 236). Decomposed by heating to 140° with water and lead oxide, forming lead bromide and methyl-ethyl ketone (Eltekow, J. R. 10, 219).

3. *Iso-tetrylene bromide*

$(CH_3)_2CBr.CH_2Br.$;

b.p. 148–149° at 737 mm.; sp.gr. $\frac{14^\circ}{} = 1{\cdot}798$ (Linnemann, A. 162, 36). From iso-tetrylene and bromine (L.; also Wurtz, A. 104, 249; Hell a. Rothberg, B. 22, 1737). By heating with water to 150° isobutyraldehyde is formed.

Tetrylene cyanide.

Isotetrylene cyanide (dimethyl succinonitrile) $CN.C(CH_3)_2.CH_2.CN$; b.p. 218–220°. By treating an aqueous alcoholic solution of potassium cyanide with isotetrylene bromide and allowing the mixture to stand for a fortnight. A colourless oil, moderately soluble in water. Heated to 150° with strong hydrochloric acid, it is decomposed into ammonia and dimethylsuccinic acid (Hell a. Rothberg, B. 22, 1737).

Tetrylene glycolchlorhydrin

$(CH_3)_2.CCl.CH_2OH$;

b.p. 137. From isotetrylene and hypochlorous acid (Butlerow, A. 144, 25). Very soluble in water.

Tetrylene glycols.

1. *Normal (α)-tetrylene glycol*

$CH_3.CH_2.CHOH.CH_2OH$;

b.p. 191–192° at 747·1 mm.; sp.gr. $\frac{0^\circ}{0^\circ} = 1{\cdot}0189$, $\frac{17{\cdot}5^\circ}{0^\circ} = 1{\cdot}0059$. From normal tetrylene bromide (Saytzen a. Grabowsky, A. 179, 332).

2. *β-Tetrylene glycol*

$CH_3.CH(OH).CH_2.CH_2OH$;

b.p. 203·5–204° (Kekulé, A. 162, 310); sp.gr. = 1·0259 (Wurtz, J. 1873, 474; Bl. 41, 362). Produced in small quantity by the reduction of dilute aqueous solution of aldehyde by sodium-amalgam (K.).

3. *Isotetrylene (γ)-glycol*

$(CH_3)_2C(OH).CH_2OH$;

b.p. 176–178°; sp.gr. $\frac{0^\circ}{} = 1{\cdot}0129$; $\frac{20^\circ}{} = 1{\cdot}003$. Produced by the fermentation of sugar in presence of tartaric acid (Henninger a. Sanson, C. R. 106, 208). Formed by heating isotetrylene bromide with potassium carbonate and water (Nevole, Bl. 27, 63); also by oxidation of isotetrylene by means of permanganate of potash in neutral aqueous solution (Wagner, B. 21, 1230).

4. *Pseudo-tetrylene glycol*

$CH_3.CHOH.CHOH.CH_3$

(symmetrical dimethyl ethylene glycol); b.p. 183–184°. Formed by heating for 6 or 7 hours 1 vol. of a symmetrical dimethyl-ethylene oxide C_4H_8O, with 3 vols. of water to 100° (Eltekow, J. R. 14, 372).

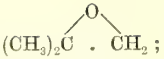
Tetrylene iodide $CH_3.CHI.CH_2.CH_2I$; sp.gr. 2·291. From β-tetrylene glycol and hydriodic acid (Wurtz, Bl. 41, 362).

Iso-tetrylene nitrite $C_4H_8(NO_2)_2$.

By treatment of isotetrylene with concentrated nitric acid (Haitinger, M. 2, 287). Forms a crystalline mass. Probably the same body was obtained by Beilstein and Kurbatow (B. 14, 1621) by treating the petroleum of Tiflis (b.p. 40–50°) with nitric acid (sp.gr. 1·52). It formed needles which melted at 96°. They were insoluble in water, but soluble in alcohol and ether.

Tetrylene oxides C_4H_8O.

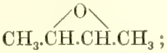
1. *Iso-tetrylene oxide*



$(CH_3)_2\overset{\frown O \frown}{C\;.\;CH_2}$;

p. 51–52°; sp.gr. $\frac{0^\circ}{} = \cdot8311$. From the chlorydrin, C_4H_9ClO, and potash (Eltekow, J. R. 14, 368).

2. *s-Dimethyl ethylene oxide*



$CH_3.\overset{\frown O \frown}{CH.CH}.CH_3$;

p. 56–57°; sp.gr. $\frac{0^\circ}{} = \cdot8344$. Formed from the hlorhydrin (prepared from the symmetrical limethyethylene and hypochlorous acid) and potash (Eltekow, J. R. 14, 371).

Tetryl chloral, butyl chloral

$CH_3.CHCl.CCl_2.CHO$.

More correctly, tri-chlor-butyric-aldehyde; b.p. 164–165° at 750 mm.; sp.gr. $\frac{20^\circ}{4^\circ} = 1\cdot3956$ (Brühl, A. 203, 20). Formed by the action of chlorine upon ordinary aldehyde, or para-aldehyde (Krämer a. Pinner, B. 3, 383). Chloracetaldehyde $CH_2Cl.CHO$ is first formed, and this condenses with another molecule of acetaldehyde, forming α-chlorcrotonaldehyde $CH_3.CH:CCl.CHO$ and water, and this, by the action of more chlorine, forms the 'tetryl chloral.'

Preparation.—Chlorine is led through cooled para-aldehyde (or aldehyde cooled by a freezing mixture); water is then added, and the liquid neutralised with calcium carbonate. The mixture is then distilled on the oil-bath in a current of steam, and the hydrate is thus obtained. This is then purified by re-crystallisation from water, and decomposed by distillation in a stream of hydrochloric acid gas (Pinner, A. 179, 26).

Butyl chloral is converted by fuming nitric acid into $\alpha_2\beta$-trichlorbutyric acid. Phosphorus pentachloride converts it into a body $C_4H_4Cl_4$, which boils at 200°. It combines with zinc-ethyl to form a compound which is decomposed by water with formation of trichlortetryl alcohol.

The ammonia compound

$CH_3.CHCl.CCl_2CH(OH)NH_2$,

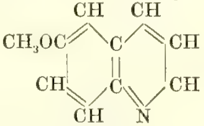
m.p. 62°, is formed by leading ammonia into a mixture cooled by ice and salt of 1 part of butyl-chloral, and $1\frac{1}{2}$ parts of chloroform (Schiff a. Tassinari, B. 10, 1783). It forms a solid mass, insoluble in water, soluble in ether, alcohol, and chloroform. Is readily decomposed on heating.

Butyl chloral has a strong affinity for water, and readily forms the *hydrate* $C_4H_5Cl_3O.H_2O$, which crystallises in trimetric plates, and which is slightly soluble in cold, and moderately soluble in hot, water; m.p. 78° (Krämer a. Pinner), 74–75° (Lieben a. Zeisel, M. 4, 533). On melting, partial dissociation is produced, so that the m.p. is lowered by long heating; sp.gr. 1·694 (Schröder, B. 12, 562). It is decomposed by distillation into the chloral and water. Alcohol and potassium cyanide convert the hydrate into α-chlorcrotonate of ethyl. Zinc and hydrochloric acid, or zinc-dust and water, produce mono-chlorcroton aldehyde, and finally crotonaldehyde (Sarnow, A. 164, 108). With acetic acid and iron filings, butyraldehyde, normal tetryl alcohol, and crotyl alcohol are produced (Lieben a. Zeisel, M. 1, 840).

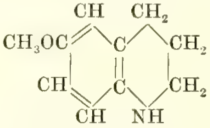
THALLINE. A base obtained from *p*-amido-anisoïl, the salts having antipyretic properties. It is prepared as follows.

78 grms. *p*-amido-anisoïl, 50 grms. *p*-nitro-anisoïl, 320 grms. of glycerin, and 125 grms. concentrated sulphuric acid are heated with an inverted condenser for 2 hours, and after this for 2 hours longer, 50 grms. of sulphuric acid having been added. The nitro-anisoïl is then blown off by means of steam, and the mixture of bases is precipitated by an alkali. From this the quinanisoïl is separated by means of its slightly-soluble acid sulphate.

Quinanisoïl has the following constitution:



is a faint yellow oil, distilling without decomposition at 186° at 35 mm., and sp.gr. 1·1402 at 20°. It forms characteristic salts, but has no antipyretic properties. It is converted by means of tin and hydrochloric acid into tetra-hydroquinanisoïl, *i.e.* thalline, this name being given on account of the green colouration which the substance and its salts gives with oxidising agents. The constitution of the body is:



Thalline dissolves with difficulty, even in hot water, but is easily soluble in alcohol, ether, and benzene. It forms thick prisms, which melt at 43°; it boils at 283° at 735 mm. The hydrochloride, sulphate, tartrate, and picrate (m.p. 162°) are all crystalline salts. The acetyl derivative crystallises in prisms which melt at 47°. Thalline also forms compounds with methyl and ethyl iodide, and with benzyl-chloride.

(Skraup, M. 6, 760; Germ. Pat. 30,426, June 18, 1884; Vulpius, Ar. Ph. 222, 840.)

THALLIUM. Sym., Tl. At.w. 203·7 (Crookes). This metal occurs to the extent of 17·25 p.c. in the rare mineral *crookesite* (CuTlAg)Se, and in small quantities in iron and copper pyrites, and in the seleniferous deposits from the sulphuric acid manufactured therefrom, in which it was discovered by Crookes by means of the spectroscope. It is also found in lepidolite, carnallite, alum, and in the mother-liquors from the Nauheim salt springs. Its presence has been observed in crude zinc (Kosmann) and in platinum and its ores (H. N. Warren).

Thallium is a bluish-white, lead-like, crystalline, extremely soft metal, malleable, but of low tenacity. Its sp.gr. is 11·8, and its m.p. 290°. At a high temperature it may be distilled in a current of hydrogen.

Thallium oxidises before the blowpipe. It dissolves readily in dilute acids, and at a red heat decomposes water. It resembles the alkali metals in many of its compounds, notably in its soluble hydrate, carbonate, and silicate, and in its power of replacing those metals in alum and other salts, but in its physical properties, its haloid salts, and its black insoluble sulphide it resembles lead.

Two oxides are known: Tl_2O, giving a soluble, strongly alkaline hydrate, and Tl_2O_3. According to Piccini, a third oxide TlO_2 exists. The salts are poisonous, and impart a green colour to the flame. Among the salts may be mentioned four chlorides: $TlCl$, Tl_2Cl_3, $TlCl_2$, and $TlCl_3$, and other haloid salts, two sulphides, Tl_2S and Tl_2S_3, a cyanide $TlCN$, nitrate $Tl(NO_3)_3SH_2O$, sulphates Tl_2SO_4 and $Tl_2(SO_4)_37H_2O$, and the soluble carbonate $TlCO_3$, and silicate.

THALLOCHLORE. A name given by Knop and Schnedermann to the green colouring matter of lichens (A. 56, 147).

THEBAINE *v.* VEGETO-ALKALOIDS.

THEINE or *Caffeine v.* VEGETO-ALKALOIDS.

THENARD'S BLUE. *Cobalt blue v.* PIGMENTS.

THENARDITE. Native anhydrous sodium sulphate.

THEOBROMA CACAO *v.* COCOA.

THEOBROMIC ACID *v.* FATTY ACIDS.

THEOBROMINE *v.* VEGETO-ALKALOIDS.

THEOPHYLLINE *v.* VEGETO-ALKALOIDS.

THERMOMETERS. Changes of temperature are measured by the corresponding alterations produced in one or other of the physical properties of a substance. Thus the expansion of solids, liquids, and gases, the vapour pressures of liquids, the electrical resistance of metals, and other properties have been utilised for the determination of temperature.

In nearly every case the amount of change produced by a given rise or fall of temperature depends on the nature of the substance, and must therefore be carefully determined beforehand for the particular material employed.

There is, indeed, only one known method of measuring temperature which is theoretically perfect, that is to say, which is entirely independent of the nature of the substance; this method, proposed by Lord Kelvin, depends on the ratio of the work done by a reversible heat engine to the heat supplied to it, and the temperature, reckoned from absolute zero, may be defined as the reciprocal of Carnot's function. The method is not one, however, that is capable of practical application.

It has been found that within certain limits of temperature and pressure the expansion of all gases is very nearly the same for equal changes of temperature. Hence it is possible to devise a method of measuring temperature which, while practically independent of the nature of the (gaseous) substance employed, is at the same time fairly convenient for many purposes. It is important also to remark that the values given by an air or gas thermometer are in very close agreement with Lord Kelvin's thermo-dynamical temperatures.

The relation of the volume of a gas to its temperature and pressure may be stated simply as follows: The volume of a gas varies inversely as the pressure and directly as the absolute temperature, or $p\,v = c\,\mathrm{T}$, where p is the pressure, v the volume, T the absolute temperature, and c a constant depending on the units chosen. If the volume remain constant the pressure varies directly as the absolute temperature, or $p = c'\mathrm{T}$, while if the pressure be kept constant the volume varies directly as the absolute temperature, or $v = c''\mathrm{T}$.

It is true that the co-efficients of expansion of different gases are not absolutely identical, and that the law holds good only within certain limits of temperature and pressure; but under pressures not greatly exceeding that of the atmosphere the deviations are extremely small in the case of oxygen, nitrogen, hydrogen, and some other gases, except at very low temperatures. It seems probable, indeed, that the hydrogen thermometer gives reliable results even below $-200°$. Wroblewski (C. R. 100, 979) states that it cannot be depended on below $-193°$, basing his conclusion on a comparison with a thermo-electric pile of copper and German silver, but Olszewski (C. R. 100, 350) employed a hydrogen thermometer in the determination of the vapour pressures of oxygen, and obtained an apparently accurate, or very nearly accurate, result at so low a temperature as $-211°$ (Ramsay a. Young, P. M. January 1886, 42).

An 'air' thermometer may be so constructed that (1) the pressure remains constant and the alteration of volume is measured; (2) the volume remains constant and the change of pressure is observed; (3) both pressure and volume are allowed to alter, and both are measured. The air or other gas is contained in a glass, or for very high temperatures a porcelain bulb, connected by means of a capillary tube with a mercury or sulphuric acid manometer. The bulb is heated to the required temperature while the other parts of the apparatus remain at the temperature of the room. If the pressure be kept constant the gas will expand, and at high temperatures a considerable portion of it will pass into the cold part of the apparatus and must be measured at the ordinary temperature; it is therefore usually considered better to raise the pressure so as to keep the volume of gas as nearly constant as possible. The vessel containing the gas expands, however, when the temperature rises, and a correction on account of this expansion must be introduced.

There are also two sources of error which are difficult to estimate, but they may be almost entirely eliminated by taking suitable precautions. The first depends on the fact that at ordinary temperatures air condenses to a slight extent as a sort of film on the surface of glass, while at high temperatures this condensed air is converted into gas, so that the apparent expansion is a little greater than the real. If, however, the bulb, after thorough exhaustion at a high temperature, be filled with air from which all moisture and carbon dioxide have been removed, the error becomes practically negligible (Callendar, Tr. vol. 178A, p. 161).

The second is due to slight changes of volume which a glass vessel is liable to undergo after being strongly heated and allowed to cool again. The magnitude of the possible error becomes extremely small, however, if the bulb be heated for some hours to at least the highest temperature which is to be registered, before its volume is determined. This point will be more fully discussed when dealing with mercurial thermometers. Of the numerous forms of air thermometers which have been devised, the three shown in the diagrams may serve as examples. The first (fig. 1) represents a form of instrument employed by Regnault in his classical researches. The bulb A of the thermometer is connected by a capillary tube (passing through a perforation in the screen B) with the mercury manometer *mm'*, a front view of which is shown in fig. 2. By addition of mercury to the open limb *m'*, or by its removal by means of the stopcock *s*, the mercury in the limb of the manometer connected with the air thermometer may be always kept at the same height, so that there is no alteration of the volume of air except that due to the expansion of the bulb when heated.

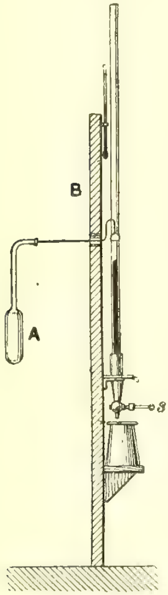


FIG. 1.

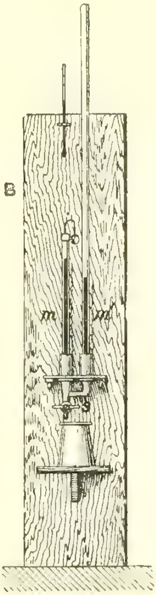


FIG. 2.

The calculation of the temperature is based on the fact that the mass of air remains constant, though its temperature, its pressure, and, to a small extent, its volume undergo change. Let

V = volume of bulb A at 0° ;

v = volume of capillary tube, together with the small portion of the manometer above the mercury in m, also at 0° ;

α = co-efficient of increase of pressure of dry air at constant volume ;

κ = co-efficient of expansion of glass ;

D = mass of 1 c.c. of air at 0°C. and 76 cms. pressure ;

P = observed pressure—that is to say, the barometric pressure, *plus* or *minus* the difference of level of the mercury in m and m'.

When the bulb is placed in melting ice, while the capillary tube and manometer are at the temperature $t°$ of the room, the total mass of air will be

$$\text{D.P.}\left\{ V + \frac{v(1+\kappa t)}{1+\alpha t} \right\}$$

When the bulb is heated to the unknown temperature x, the temperature of the capillary tube and manometer being now t', the mass of air will be

$$\text{D.P.}'\left\{ \frac{V(1+\kappa x)}{1+\alpha x} + \frac{v(1+\kappa t')}{1+\alpha t'} \right\}$$

Therefore

$$P\left\{ V + \frac{v(1+\kappa t)}{1+\alpha t} \right\} = P'\left\{ \frac{V(1+\kappa x)}{1+\alpha x} + \frac{v(1+\kappa t')}{1+\alpha t'} \right\}$$

an equation in which everything is known but x.

The value of α determined by Regnault is 0·003665, but the fraction $\frac{1}{273}$ is very nearly correct, and is frequently employed.

If the volume of air be allowed to vary, the limb m of the manometer must be graduated, and should be surrounded by cold water of known temperature. In this case the additional volume v' at the temperature of the water must be brought into the equation.

Sulphuric acid may be employed with advantage in place of mercury, since it moves more freely in a narrow tube, and, being lighter, allows of more delicate readings ; or a small sulphuric acid gauge may be interposed between the thermometer and the mercury manometer. An apparatus which can be employed either as a constant volume or constant pressure manometer has been described by Callendar (*l.c.*) and more fully by Callendar and Griffiths (Tr. vol. 182A, 119). It is represented in fig. 3.

When the measurement is to be made at constant volume the mercury in A is brought up to the zero point, and the stopcocks T_2 and T_3 are closed. The level of the sulphuric acid in the gauge is then regulated by means of an ordinary mercury manometer, not shown in the diagram, and the pressure is the algebraical sum of the barometric pressure, that registered by the mercury manometer, and the slight difference in level, if any, of the sulphuric acid in the two limbs of the gauge FK, divided by the specific gravity of mercury compared with that of sulphuric acid.

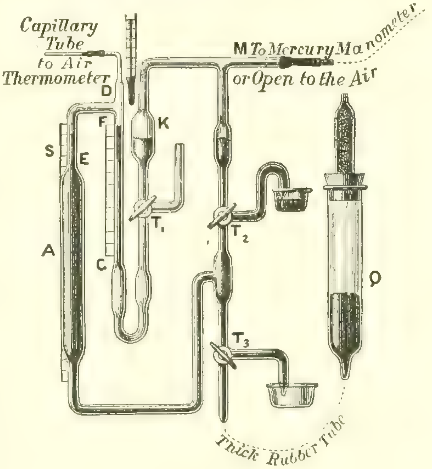


FIG. 3.

If the pressure is to be kept constant, the tube A is first filled from the reservoir Q until the level of the mercury stands at some point in the tube DE, recorded by the scale S, the pressure of the air in the bulb being equal to that of the atmosphere, as shown by the sulphuric acid gauge. (In this case the tube M is not connected with the mercury manometer, but is open to the air.) When the bulb is heated, mercury is allowed to escape by the three-way tap T_3 into the weighed beaker, the tap being closed as soon as the sulphuric acid gauge indicates that the pressure is again equal to that of the atmosphere. The increased volume is calculated from the weight of mercury expelled. The narrow tubes DE and FG are calibrated and provided with scales. For the advantages of the sulphuric acid gauge see also Bottomley (P. M. 1888 (Aug.), 149).

Callendar has quite recently described a modified constant-pressure air thermometer which appears to possess marked advantages over those previously devised, and gives extremely accurate results. The pressure of the air in the thermometer is not adjusted to equality with that of the atmosphere, but always with the same constant pressure, obtained by connecting the outer limb of the sulphuric acid gauge to a glass bulb filled with air and kept in melting ice.

The effect of changes of temperature of the connecting tubes on the readings is entirely eliminated by the employment of compensating tubes of the same size, and thus the troublesome and somewhat uncertain correction hitherto necessary is obviated. The compensation is perfect when (1) the two sets of connecting tubes are of equal volume and at the same mean temperature; (2) the mass of air inclosed in the standard pressure-bulb is equal to that in the thermometric and mercury bulbs; (3) the pressures are adjusted to equality. Under these conditions, the temperature of the thermometer bulb (on the air-thermometer scale) is given by the simple equation $\theta_1 = V_1\theta_0/(V_0 - Vm)$, where V_1 is the volume of air in the thermometer bulb at θ_1°, V_0 and Vm are the volumes of air at 0°C. in the standard pressure bulb and the mercury reservoir (this being also surrounded by melting ice), and θ_0 is the temperature of melting ice on the air-thermometer scale.

For moderate ranges of temperature, and when extreme accuracy is not required, the apparatus may be greatly simplified, and may be so constructed that the temperatures are read directly on the sulphuric acid gauge; it is stated that such thermometers can be made to read to the tenth of a degree at 450°. This form of direct reading thermometer has been patented and is recommended for technical purposes.

Other forms of air thermometer have been described by Balfour Stewart, Tr. 153, 425; Codazza, D. P. J. 210, 255; Jolly, Pogg. Jubelband, p. 82; Mitscherlich, A. 12, 146; Crafts, A. Ch. [5] 14, 409; Andrews, B. 14, 2116; Pettersson, J. pr. [2] 25, 102; Cailletet, C. R. 106, 1055; Berthelot, A. Ch. [4] 13, 144. A platinum bulb was recommended by Pouillet (C. R. 3, 782), but it was pointed out by Becquerel (A. Ch. 58, 49) that at high temperatures air passes through the platinum. A porcelain bulb was employed by Weinhold (P. 149, 188), by Deville and Troost (A. Ch. [3] 58, 265), and others.

Air thermometers for technical purposes are generally provided with scales which are calibrated empirically by heating the bulbs to two or three known temperatures, so as to obtain a certain number of fixed points. The scales are then constructed by interpolation.

Thermometers of this class have been described by P. Schoop, Germ. Pat. 20,345 (1882); Witz, C. R. 91, 164; Beilby, S. C. I. 1885, 41; Coleman, *ibid.* 1885, 43, and by Heisch and Folkard. The last of these is very simple, and has been found by Hurter (*ibid.* 1886, 635) to give good results. The bulb A (fig. 4) contains air under reduced pressure, and there is a vacuum over the mercury in the manometer M.

For ordinary purposes the mercurial thermometer is the most convenient, for it may be made of any required size, it is easily portable, and the bulb, if elongated, need not be wider or, indeed, so wide as the stem. The instrument consists of a spherical or cylindrical bulb fused to a capillary tube of suitable length. The bulb is filled with pure mercury, which must be boiled for some time to remove the film of gas or aqueous vapour which adheres obstinately to the surface of the glass. If the thermometer is required for low temperatures only, there is usually a vacuum in the stem of the thermometer, but for high temperatures it is necessary to fill the capillary tube with nitrogen to prevent distillation of the mercury, a small bulb being blown at the upper end of the tube in order that when the mercury expands and compresses the nitrogen the pressure shall not rise too high.

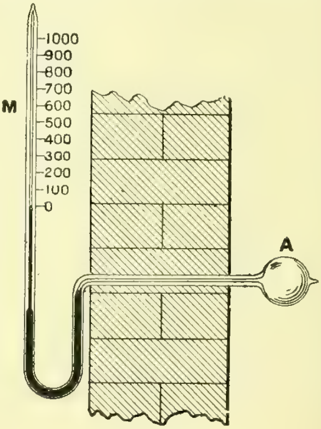


FIG. 4.

An ordinary thermometer is graduated by placing it *first* in the steam from water boiling under known pressure and then in melting ice (*v.* Guillaume, Traité pratique de la Thermométrie de Précision, p. 112). The variation of the melting-point of ice with the pressure is so minute that this point may be taken as absolutely fixed, but the boiling-point of water varies considerably with the pressure, and therefore some standard pressure must be chosen. This is 760 mm. or 29·922 inches of mercury measured at 0°C. and at the latitude of Paris for the Centigrade scale, and 29·905 inches of mercury at 32°F. at the latitude of London for the Fahrenheit scale.

The position of the mercury in the stem is marked off at these two temperatures, and the space between these two fixed points is then usually divided into a certain number of equal parts—100 on the Centigrade scale, 180 on the Fahrenheit, and 80 on the Réaumur. On the Centigrade and Réaumur scales the melting-point of ice is taken as the zero point, but on the Fahrenheit the zero of the scale is placed 32 divisions lower down, so that the melting-point of ice is 32°, and the boiling-point of water 212°.

A thermometer graduated in this manner does not, however, register true temperatures except at the two fixed points, for the following reasons:—1. It is impossible to obtain an absolutely cylindrical capillary tube, so that the volume corresponding to a scale division is not quite the same in all parts of the tube. Various methods have been devised for calibrating the stem (*v.* Brit. Assoc. Report, 1882, 145-204, also Guillaume, *l.c.* pp. 43–99), but when this is done there remain other sources of error. 2. The position of the mercury in the stem at any temperature depends on the expansion both of the mercury and of the glass, and in each case the rate of expansion increases with rise of temperature. Moreover, different kinds of glass have different rates of expansion, so that two thermometers made of different materials—even if the capillary tubes were perfectly cylindrical—would give different readings at the same temperature. The only really satisfactory method of correction of such a thermometer is to compare its readings either directly with an air thermometer, or with another mercurial thermometer which has previously been standardised by means of an air thermometer. Or a number of fixed points may be determined by heating the thermometer with the vapours of a series of pure liquids boiling under known pressures. The following table contains a list of suitable substances with their boiling-points, and the variation of pressure corresponding to 0·1°C. at the boiling-points:—

Substance	Boiling-point at 760 mm. at 0°.	Variation of Pressure for 0·1C.	Observer and Reference
	°	mm.	
Carbon bisulphide . .	46·20	2·48	Regnault, Mémoires, 26, 658.
Ethyl alcohol . . .	78·26	3·05	,, ,, ,,
Water	100·00	2·71	,, ,, 21, 633.
Chlorobenzene . .	131·95	2·02	Ramsay a. Young, C. J. 47, 640.
Bromobenzene . .	156·15	1·94	,, ,, ,, ,,
Aniline	184·4	1·96	,, ,, ,, ,,
,, ...	184·13	—	Callendar a. Griffiths, Tr. 182A, 151.
Naphthalene . . .	218·05	1·72	Crafts, Am. 5, No. 5.
,, . . .	217·94	—	Callendar a. Griffiths, *l.c.*
,, . . .	218·04	—	Griffiths, Tr. 182A, 152.
Methyl salicylate . .	222·90	1·75	Ramsay a. Young, *l.c.*
,, ,, . .	223·03	—	Callendar a. Griffiths, *l.c.*
Quinoline . . .	237·45	1·70	Young, C. J. 55, 483.
Bromonaphthalene .	280·45	1·57	Ramsay a. Young, *l.c.*
Benzophenone . .	306·08	1·58	Crafts, *l.c.*
,, . .	305·82	—	Callendar a. Griffiths, *l.c.*
Dibenzyl ketone . .	330·55	1·52	Young, C. J. 59, 626.
Mercury	356·83	1·33	,, ,, 59, 629.
,, ...	356·74	—	Callendar a. Griffiths, *l.c.*
Sulphur	444·53	(about) 1·15	,, ,, ,, Tr. 182A, 145.

In this way a table or curve of corrections may be constructed showing the error at any scale reading of the thermometer. 'Normal' thermometers may now be purchased; they are compared with a standard thermometer before graduation, and true temperatures are stated to be registered by them.

Tables of correction of readings of mercurial thermometers to true air-thermometer temperatures have been published by various observers; but as these tables must necessarily vary for different kinds of glass—the further correction for unevenness of bore being also required—they do not seem to possess much *general* value. It may be useful, however, to give references:—Rudberg, A. 36, 121; Bosscha, C. R. 69, 875 and 1185; Regnault, C. R. 69, 879 and Mémoires, 21, 239; Crafts, C. R. 95, 836; Recknagel, P. 123; Guillaume, Traité pratique de la Thermométrie de Précision.

Even when the above corrections to true air-thermometer temperatures have been made, there remain some sources of error, the most important of which is the alteration of the capacity of the bulb, and doubtless also of the capillary tube after long-continued heating, and, indeed, after any considerable change of temperature. A vast amount of experimental work has been done on this subject, and the explanation of the observed changes has given rise to a great deal of discussion. The following references may be made to the literature of the subject:—Despretz, C. R. 4, 926; Person, *ibid.* 19, 1314; Legrand, *ibid.* 4, 173; Crafts, *ibid.* 91, 291, 370, and 413; 94, 1298; Pernet, *ibid.* 91, 471; E. J. Mills, T. Ed. 29, Part 2, 587, and Nature, 41, 100, 227, and 538; Young, *ibid.* 41, 152, 271, 488; Tomlinson, *ibid.* 41, 198; Pernet, Travaux et Mém. du Bureau Int. des Poids et Mesures, vol. i., B. p. 52, and I., p. 17; Guillaume, Traité pratique. The most important facts regarding the alteration of zero point may be shortly described as follows:—

1. If a thermometer be graduated shortly after the bulb has been blown, the zero point will rise with comparative rapidity at first, then more and more slowly, and the elevation of the zero point may go on for many years. Joule (Scientific Papers, i. 558) took observations with one thermometer over a course of thirty-eight years, and the change, which then amounted to almost exactly 1°F., was still proceeding.

2. If a thermometer be maintained at a high temperature for a considerable time, the rise of the zero point takes place with much greater rapidity, and up to, at any rate, 360°, and probably 450°, the higher the temperature the more rapid is the rise, and *apparently* the higher is the final point reached. A total elevation of over 20° has in several cases been observed, while larger glass bulbs, after continuous heating to 445°, or in one case 511°, have been found by Regnault, Crafts, and Callendar and Griffiths to suffer a contraction of from 0·25 to 0·34 per cent. In all cases the rise or contraction, which is rapid at first, becomes slower and slower, and it seems doubtful whether at any given temperature actual constancy of zero point or capacity has ever yet been attained. If, however, a thermometer has been heated for many hours to a given high temperature and then allowed to cool very slowly, subsequent heating to lower temperatures has very little effect on the zero point, and it is advisable to subject a thermometer to this process before determining the fixed points.

3. Not only is the zero point liable to change, but the interval between the zero and 100° points may at the same time be increased, for the coefficient of expansion of glass suffers diminution after prolonged heating.

4. Internal or external gaseous pressure on the bulb appears to have little or no influence on the rise of zero point.

5. If a thermometer—even after its zero point has been rendered as permanent as possible — be heated and then cooled very rapidly, a fall of the zero point will be observed, but after a day or two the greater part of this fall will be recovered, and the remainder after a longer period.

Other possible sources of error are the following:—If the mercury in the stem of the thermometer—or a portion of it—be not heated to the same temperature as that in the bulb, a correction is required. This point has been discussed in the article on Distillation, vol. i., p. 688.

The bulb is slightly compressible, and considerable changes of external pressure may affect the readings to some extent.

Mercury does not move very freely in a capillary tube, and in delicate thermometers, when the temperature changes, the movement of the mercury may take place in jerks instead of smoothly. This may be avoided by tapping the thermometer (Pickering, P. M. 1886, vol. xxi.).

For temperatures below −38·8°, the freezing-point of mercury, an alcohol or toluene thermometer may be employed. The liquid alloy of potassium and sodium has also been used as a thermometric substance for temperatures above the boiling-point of mercury.

Special forms of the mercurial thermometer suited to technical purposes, in which ebullition of the mercury is prevented by increased pressure even at very high temperatures, have been devised by Murrie (S. C. I. 1885, 45, 189, 655).

Other Forms of Thermometer.

Platinum resistance thermometer. The measurement of temperature by the alteration of the resistance to electricity of a platinum wire was suggested by Siemens (Bakerian Lecture, Pr. 1871), but in consequence of an adverse report to the British Association in 1874 this method was abandoned. Recently, however, the subject has again been investigated by Callendar (Tr. 178; A. 161), Griffiths (*ibid.* 182; A. 43), and both authors (*ibid.* 182; A. 119), with very satisfactory results. In order to insure accuracy the platinum wire must be pure in the first place; it must be prevented from alloying with silicon, carbon, tin, or other impurities, and it must not be subjected to strain—such as elongation. When these conditions were fulfilled, the resistance of a wire was always found to be constant at a given temperature. The form of thermometer recommended by Callendar and Griffiths is shown in fig. 5. Two platinum wires are interwound in a double-screw thread, passing through holes in a thin mica plate A B. Each spiral is provided with a double and single electrode, symmetrically arranged. The six electrodes are insulated, and kept in place by passing through holes in thin mica wads (one of which is shown at C) which are cut to fit the glass tube containing the thermometer. The electrodes are best made of platinum, the ends of the wires being fused to them by the oxyhydrogen flame. For temperatures up to about 500° the spirals may be wound round ignited asbestos, but the insulation becomes imperfect at higher temperatures.

If $R_0 R_1$ be the resistances at 0° and 100°C., and R that at any other temperature, the corresponding value of the 'platinum' temperature *pt* is deduced by the formula

$$pt = 100\ (R - R_0)/(R_1 - R_0).$$

For details as to the method of operation, comparisons of the platinum with the air thermometer, and the degree of accuracy attainable, the original papers should be consulted. See also Callendar, P. M. 32, 104; Spohr, D. P. J. 257, 315.

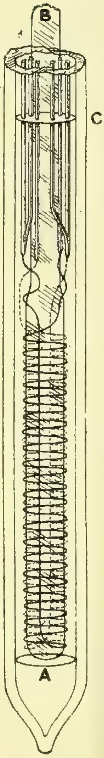


Fig. 5.

Vapour pressure thermometer. This form of instrument has been recommended by Lord Kelvin (Pr. E. 1880, 432), and has been introduced into practice under the name of the 'Thalpotassimeter' by Schäffer and Budenberg (Dittmar, S. C. I. 1885, 44). If the vapour pressures of a given liquid have been accurately determined through a certain range of temperature, any temperature within these limits may be afterwards determined by observing the pressure exerted by the vapour of the liquid.

The method possesses the great advantage that alteration of the capacity of the vessel containing the liquid and vapour is entirely without influence on the pressure, which is solely dependent on the temperature.

Probably the most serious objection to the method is the difficulty of filling the vessel or reservoir with the pure liquid *entirely free from air*, and if this difficulty be not overcome large errors may be introduced. In the case of the thalpotassimeter, it appears also that leakage gradually takes place, so that the liquid escapes after a time. The apparatus is necessarily also somewhat cumbersome. For high temperatures, however, a mercury vapour pressure thermometer is sometimes serviceable, and may be arranged as in fig. 6 (Ramsay a. Young, C. J. 47, 651). The mercury must be well boiled to remove the film of air adhering to the glass, but this may be done without much difficulty.

Thermometers constructed to measure extremely high temperatures are known as pyrometers. Probably the most accurate results are to be obtained with the porcelain air thermometer and the platinum resistance thermometer. Other methods which have been proposed or adopted are the following:—

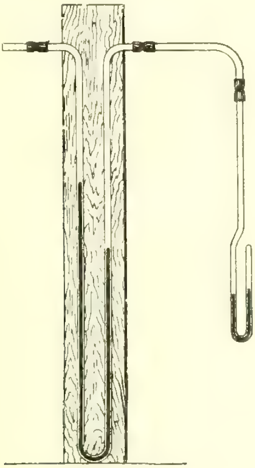


Fig. 6.

1. The measurement in a calorimeter of the amount of heat evolved by a piece of platinum on cooling from the high temperature to the final temperature of the water in the calorimeter.

Let x be the unknown high temperature; t, the initial temperature of the water in the calorimeter; θ, its final temperature; M, the mass of water, plus the water equivalent of the calorimeter; m, the mass of platinum taken, and s, the specific heat of platinum. Then, since $ms\,(x-\theta)=\mathrm{M}\,(\theta-t)$

$$x=\frac{\mathrm{M}\,(\theta-t)}{ms}+\theta.$$

The specific heat of platinum, like that of other metals, increases with rise of temperature, so that s, which should be the mean specific heat between x and θ, depends really on the former of these temperatures, and a troublesome calculation is required in order to obtain an accurate result. Taking $s=0{\cdot}036$, however, a preliminary rough calculation of the temperature x may be made, and then from the following table a more accurate value of s may be obtained and the calculation repeated.

Mean Specific Heat of Platinum (Pouillet).

Between 0° and 100°C. .	. 0·0335
,, 0° ,, 300°C. .	. 0·0343
,, 0° ,, 500°C. .	. 0·0352
,, 0° ,, 700°C. .	. 0·0360
,, 0° ,, 1000°C. .	. 0·0373
,, 0° ,, 1200°C. .	. 0·0382

Codazza gets over the difficulty by employing two pieces of platinum of different weights, m_1 and m_2; then, the initial temperature of the calorimeter being the same in both cases, the final temperatures θ_1 and θ_2 will be different. Calling the quantities of heat $\mathrm{M}(\theta_1-t)$ and $\mathrm{M}(\theta_2-t)$, Q_1 and Q_2, we have $\mathrm{Q}_1=sm_1(x-\theta_1)$, and $\mathrm{Q}_2=sm_2(x-\theta_2)$; hence s may be eliminated, and

$$x=\frac{\mathrm{Q}_1m_2\theta_2-\mathrm{Q}_2m_1\theta_1}{\mathrm{Q}_1m_2-\mathrm{Q}_2m_1}.$$

References.—Pouillet, C. R. 3, 786; Weinhold, P. 149, 216; Violle, P. M. [5] 4, 318.

2. The employment of a series of pure salts, the melting-points of which are known (Carnelley, C. J. vol. 33; Carnelley a. Williams, *ibid.* vols. 33, 35, 37). It is possible in this way to ascertain that a given temperature lies between the melting-points of two salts in the series. It has also been proposed to employ alloys of gold and silver, or gold and platinum, in a similar manner (Tr. 1828, 79).

3. The determination of the weight of mercury vapour in a hard glass or porcelain bulb (Regnault, Mémoires, 21, 267).

4. The expansion of a rod of metal or other solid substance, or the difference in expansion of two solid substances; or, again, the coiling or uncoiling of a spiral composed of two or more metals rolled or welded together to form a ribbon. Daniell's well-known pyrometer (P. 39, 577) and Breguet's metallic thermometer belong to this class; *v.* also Ochsle, A. 20, 140; Breguet, C. R. 5, 720, and 16, 210; Hurter, S. C. I. 1886, 635.

5. The measurement of the permanent contraction of clay (Wedgwood, Tr. 1782, 1784, and 1786).

6. The passage of a moderately-rapid current of cold water through a protected metal tube placed in the furnace or heated chamber. The arrangement described by Amagat (C. R. 97, 1053) appears to be the best. The tube is bent in the form of a spiral so as to increase the length, and the rate of current is regulated by the head of water, which is easily kept constant. A pyrometer of this kind may be so arranged that a rise of 10° in the temperature of the water corresponds to 1000° in the furnace.

For further remarks on pyrometers *v.* D. P. J. 225, 272; Weinhold, P. 149, 186; also Hurter (*l.c.*).

One other method of measuring temperature should be mentioned; it is based on the fact that if pieces of two different metals are joined at their extremities, and if the two junctions are heated to different temperatures, a current of electricity will as a rule be produced. If then the temperature of one junction and the strength of the current are measured, the temperature of the other junction may be ascertained. An instrument constructed on this principle is called a thermopile. Rossetti, A. Ch. 1878; Becquerel, *ibid.* 58, 49; Regnault, Mémoires, 21, 241; Tait, T. Edin. 27; Roberts-Austen, Nature, 45, 535.

S. Y.

THERMONATRITE. *Monohydrated sodium carbonate* $Na_2CO_3.H_2O$.

THERMOSTATS. A thermostat may be defined to be an apparatus so arranged as to maintain the temperature of a space constant between certain definite limits. Previous to 1860 the forms of apparatus adopted were few and simple; but, with the refinement of physical and chemical experimental methods, a need has arisen for instruments of a trustworthy character. To satisfy this need many arrangements have been suggested, which may be classed in the following groups:—

I. Thermostats depending on a flow of heated liquid for the maintenance of a constant temperature.

II. Thermostats utilising the latent heat of the alteration of the state of aggregation of a body:
  (*a*) Those in which the change is from solid to liquid;
  (*b*) Those in which the change is from liquid to vapour.

III. Other thermostats which are not self-regulating.

IV. Self-regulating thermostats, including—
  (*a*) Mercurial or other single-liquid thermometers:
    1. Acting directly on the gas supply or other heat source;
    2. Acting on the source of heat through electrical arrangements;
    3. Acting on the source of heat through mechanical arrangements;
  (*b*) Gas thermometers:
    1. Acting on the gas supply by transmission of pressure through a liquid column;
    2. Acting through electrical arrangements;
    3. Acting through mechanical arrangements;
  (*c*) Vapour-tension thermometers:
    1. Air and vapour;
    2. Vapour in contact with its own liquid only;
  (*d*) Thermostats depending on the differential expansion of solid substances;
  (*e*) Other mechanical regulators.

I. *Thermostats depending on a flow of heated or cooled liquid for the maintenance of a constant temperature* have been devised by Dupré and Page (T. 159, 608, 1869); by Stricker and Burdon Sanderson; Hinrichsen and Roth (W. 8, 83; 11, 1); and Chappuis (W. 12, 167). The form of apparatus invented by C. Blaufus-Weiss may be adapted for use either as a pressure or temperature regulator (Germ. Pat. 43,574, 7 Dec. 1887). As used in the latter capacity, it consists essentially of a cylindrical valve controlling the supply of hot or cold currents of either liquid or vapour to a worm arranged in the vat to be maintained at a uniform temperature. The valve is formed by an elliptical slit in a sheet cylinder which passes half round the circumference of the cylinder, and, when the latter revolves, is brought more or less opposite to tubes opening into the sides of the drum, which serves as a valve-box. The space within the revolving cylinder is furnished with tubes passing through the head of the drum to serve as supply or exit pipes. The valve is worked by the rise and fall of a vertical piston, actuated by the expansion and contraction of a body of mercury, which is contained in a bell-shaped vessel of which the wider end is applied to a small chamber which forms a side continuation of the vat. The vertical movement of the piston is transformed into the circular motion of the valve in a horizontal plane by means of a pin working in a screw slot on a hollow cylinder.

II. *Thermostats in which a constant temperature is maintained by the use of substances changing their state of aggregation at the required temperature.*

(*a*) For temperatures below 0°C., Wild used the cryohydrates of Guthrie. In this case, as in the ice-bath, the change of state is from solid to liquid.

(*b*) More commonly the change of state is from liquid to vapour. The vapour from a liquid boiling at the required temperature is caused to surround the oven or bath to be heated. Here the temperature will vary according to the pressure under which the liquid is boiled.

The liquids used for this purpose are:—Water, ether, methyl and ethyl alcohols, benzene, toluene, acetic acid, carbon bisulphide, amyl alcohol, xylene, turpentine, aniline, naphthalene, glycerin, diphenylamine, the monohydrate of sulphuric acid, mercury, paraffin, sulphur, zinc.

The temperatures so obtained lie between 22° and 1040°. At the ordinary atmospheric pressure one definite temperature is obtained for each substance used. Intermediate temperatures may be obtained in several ways:—(1) The pressure under which the vapour is formed is varied; (2) mixtures of liquids in various proportions are used; (3) a solid is dissolved in a liquid, the boiling-point being thus raised, and the vessel or bath is surrounded by the boiling liquid.

Alluard has used the method of boiling liquids at reduced pressures to obtain temperatures between 30° and 300°C. (C. R. 59, 500). Pfaundler has used similar means (Sitz. B. [2] 56, 1867).

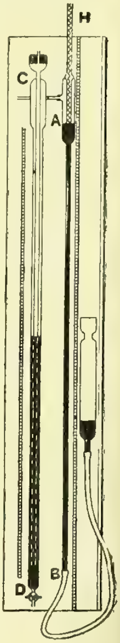


Fig. 1.

L. Meyer devised an apparatus for determining the boiling-point of a liquid at any pressure below that of one atmosphere. It may be used to control a constant-temperature bath (A. 15, 303). The apparatus (see fig. 1) is a pressure control valve. The mercury in AB cuts off the connection with the air-pump through H as soon as the pressure is reduced to the required point; CD is a mercury valve which admits air to the apparatus immediately the pressure falls below that fixed upon.

Brown has improved this apparatus, rendering it possible to use it for pressures higher, as well as lower, than one atmosphere. A mercury manometer is so constructed that, immediately the pressure falls below or rises above that determined upon, an electro-magnetic clutch, actuating a suitable stopcock, is placed in a battery circuit, and thus connection is made between the reservoir and the pump or outer air, as may be required for adjustment (P. M. [5] 45 ; vii. 411).

Alluard has used mixtures such as the following: Ether and carbon bisulphide; carbon bisulphide and alcohol; and alcohol and water, to obtain constant temperatures in jacketed baths (C. R. 58, 82).

Reynold has similarly used mixtures of glycerin and water (Z. 1862, 213).

Sulphuric acid of various concentrations has been used by L. Hämmerle, with which temperatures ranging from 40–317·35°C. have been obtained, using varying pressures (Sitz. B. 2, 1869).

Sprengel made a sulphuric acid bath of lead, shaped after the common steam-jacketed air-baths (C. J. 11, 458).

Laspeyres constructed a sulphuric acid bath from an Erlenmeyer's flask, using a test tube for the heated chamber (see fig. 2). A platinum apparatus (fig. 3) has been described by the same author (P. 152, 132).

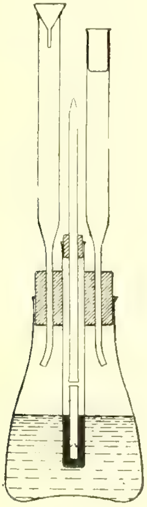


FIG. 2.

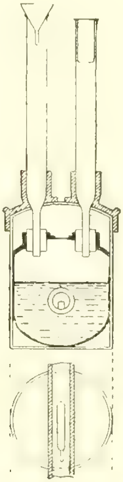


FIG. 3.

A. Fock has constructed a very serviceable bath, in which common petroleum is used as the mixture of liquids of different boiling-points. A double cylinder A B (fig. 4), serving as a vapour-jacketed bath, is connected by means of the side tubes a and b with the reflux condenser G. The tube c connected with the condenser communicates, through the stopcock r and tube d, with the reservoir flask K. A mixture of liquids (*e.g.* common petroleum) is placed in the bath and distilled, the distillate passing through the open stopcock r into the flask K. At the moment when the required temperature is attained, as indicated by the thermometer T, the stopcock r is closed; the distillate now returns through the tube b to the bath, hence the temperature of B will remain constant for any length of time (B. 18, 1124A, 1885).

Ramsay has used a vapour-bath in which the temperature is controlled by regulating the pressure under which a selected pure liquid is boiled (C. J. 1885, 640).

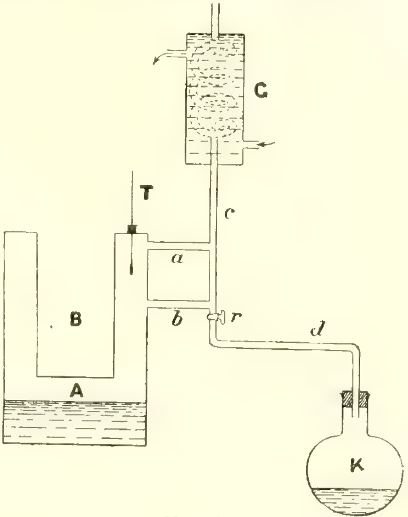


FIG. 4.

III. *Thermostats which are not self-regulated.* Instruments serving as indicators only have been devised by Hall (Q. J. Sci. 5, 52, 1818); Doyère (A. Ch. [3] 28, 5, 1850); A. Fraser (Jour. Gas Lighting, 38, 798, 1881); J. Barnes (C. J. 39, 463, 1881); A. V. Harcourt (Pr. 34, 166, 1882); U. Kreusler (Chem. Zeit. 8, 1321); and C. Winkler (B. 18, 2533, 1885).

G. Merryweather, in 1833, devised an ingenious form of apparatus for obtaining a fairly constant supply of heat by the combustion of alcohol vapour, in presence of glowing platinum foil, without flame (D. P. J. 49, 255; Mechanics' Magazine, 507, 56).

Bunsen's thermostat is a sheet-copper vessel, about 40 cm. long, of elliptical section. It is provided at equal intervals along its length with seven pairs of solid copper rods, 7–8 mm. in diameter, riveted and brazed into the sides. The outer ends of each pair project through the chimneys of as many burners, from which they serve to conduct the heat to the heated vessel. The temperature is regulated by moving the burners away from or towards the thermostat. It is essential that the apparatus be screened from draughts, that the flames be maintained of nearly the same size by a gas regulator, and that both rods be well immersed in the flame of each burner (A. 141, 273).

Exner's thermostat is of especial value, as it allows of constant temperatures being maintained between 0° and 10°C. (see fig. 5). It consists of an inner flask, surrounded by two concentric glass vessels, with an air space between; the three vessels are fastened above to a zinc plate.

A delicate thermometer and a thermo-element are placed in the centre of the flask; the stem and wires pass through a leaden pipe attached to the zinc plate. Between the two surrounding vessels is coiled a German-silver wire, the coils hanging freely without contact with either vessel; wires pass from the coil to a battery through the leaden tube. The whole is completely immersed in melting ice, contained in a fourth vessel; the leaden tube alone projects, and serves to keep the wires from contact with the ice. By passing an electric current through the German-silver coil, the temperature of the central vessel can be maintained at any desired point above 0°C. (Sitz. W. 68, 2, 1873).

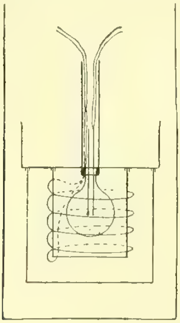


Fig. 5.

The same principle is applied by H. Crew (P. M. [5] 33, 89). The accompanying illustration (fig. 6) shows the points in which this instrument differs from the preceding one. Julien storage cells are used as the source of a constant current, which is regulated by alteration of the length of a resistance wire r, through which the current flows, by means of a slider s, and controlled by means of a Thomson balance.

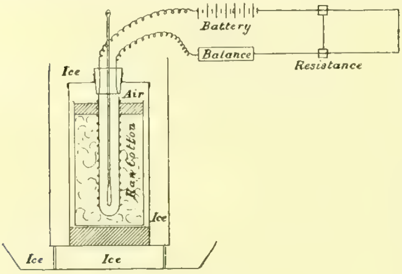


Fig. 6.

IV. *Self-regulating thermostats*: (*a*) *Single-liquid thermometers* (1) *acting directly on the gas supply* have been devised by Carmichael (Fr. 10, 85) and by Hannay (M. S. [3] 16, 1021).

Milne-Edwards, on the same principle, arranges the contracted end of the burner gas-supply tube near to the upper surface of mercury in a small reservoir connected vertically with a peculiarly made mercury thermometer; expansion of the mercury partially or wholly closes this tube, gas can then only reach the burner through a minute orifice in the leading tube (A. Ch. [4] 25, 390).

Reichert's form of regulator is essentially that of a mercury thermometer, with a reservoir at the top of the column. The gas-supply tube is placed so that its contracted opening is vertically over and near to the surface of the top of the mercury column. The leading tube takes off gas at the side of the reservoir. A small side tube on the stem is supplied with a screw by means of which the mercury level may at any time be adjusted, and the temperature maintained thus altered at will (fig. 7) (Fr. 11, 34; P. 144, 467).

Gerhardt's modification allows of easily filling the instrument with mercury.

Regulators of the same type, but varying somewhat in form, have been constructed by Page (C. J. 1876, 24), Fletcher (C. J. 1876, 488), and Roulin (D. P. J. 227, 263). The instrument devised by Roulin is constructed of iron and steel (*v.* fig. 8). The height of the mercury column is adjusted by means of a sliding tempered-steel rod, held in position by the set screw *f*. As this rod passes down the centre of the gas-supply tube, the gas can only reach the burner tube by passing through the ring-shaped aperture *d*, near the surface of the mercury. A small tap *g* maintains a sufficient supply of gas to the burner to avoid extinction of the flame by the complete interruption of the supply at *d* (D. P. J. 227, 263).

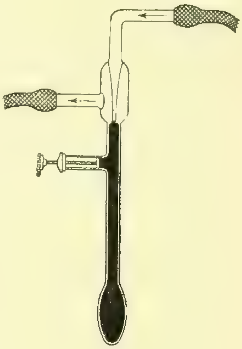


Fig. 7.

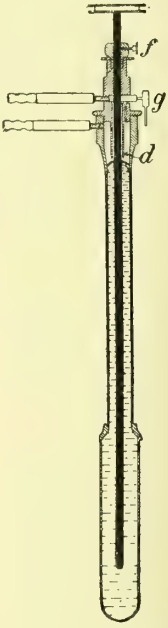


Fig. 8.

A low-temperature thermo-regulator, arranged by F. W. Dafert, serves to control the heating to a constant temperature of quantities of water (see fig. 9). The water is heated in the coil A by a burner B furnished with a chimney. The gas supply is controlled by a regulator C immersed in the heated water. The hot water passes through G, and is delivered into the reservoir near H, the supply tube for cold water, the supplies being controlled by the cocks K and L respectively. The whole mass is thoroughly mixed by a stream of air bubbles delivered through the tube F. The water required for use is drawn off from N, and, if necessary, from M.

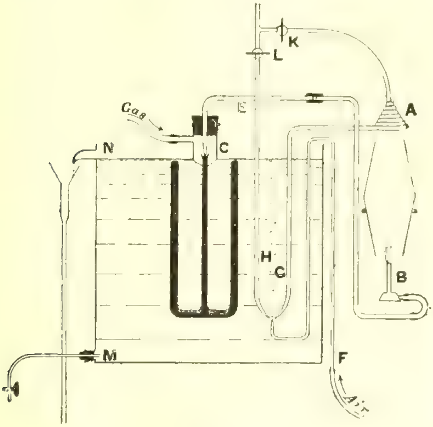


Fig. 9.

The regulator differs from that of Reichert in that the mercury reservoir is arranged with two branches reaching to the top of the water vessel; and, again, the gas proceeds to the burner through the tube E, whose narrowed extremity forms a valve with the mercury surface, instead of by means of the side tube (Chem. Zeit. 1886, 52, 789).

2. *Thermostats acting on the source of heat through electric arrangements* have been constructed by Maistre (C. R. 1854, 24), Clerget (D. P. J. 134, 23), Pfaundler (Carl's Rep. 18, 443), Salet (Bl. 1865), and Morin (C. R. 1864, 59, 1082).

Kohlrausch arranged an electric thermometer, to control the temperature of a hothouse, with two electro-magnets in the circuit of a constant battery. (Fig. 10) E$_1$ opens the hot-air valve O$_1$ if the temperature fall below 15°; if 18° be reached, the second magnet E$_2$ opens the cold-air valve O$_2$ (D. P. J. 389, 175).

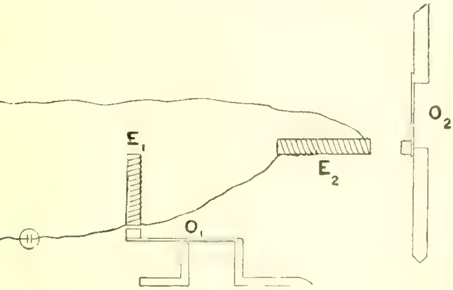


Fig. 10.

Scheibler has constructed an electro-thermostat, with the usual form of electric thermometer (fig. 11). The electro-magnet is contained in the square box A; the upper end of the armature is provided with a leather pad, which works against the continuation of the gas-supply tube *b*, and with it forms a valve which cuts off the gas when the mercury comes into contact with the upper platinum wire. The extinction of the flame is avoided by having a small hole at *c* in the tube *b*, more or less closed by means of the screw *d*, through which a small stream of gas can escape into the box, and hence into the burner tube (Fr. 1868, 88).

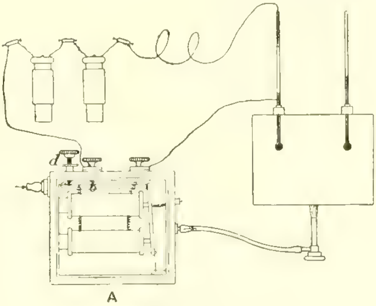


Fig. 11.

Zabel has adapted the same principle to the use of either a spirit lamp or gas flame. A shield is automatically interposed or withdrawn from between the flame and the bath (Fr. 7, 1868).

3. *Thermostats acting on the source of heat through mechanical arrangements* have been devised by Schlösing (A. Ch. [4] 19, 205; B. 5, 859), N. A. Randolph (Jour. Franklin Institute, 116, 465, 1883), V. H. Veley (C. J. 43, 370), Randall, and others. Randall's apparatus (D. P. J. 224, 478) is adapted to the heating of large masses of water to a constant temperature by the use of steam. In fig. 12 *b* is a thin-walled tubular vessel containing some expansible liquid, the movements of the surface of which are followed by the piston K. This piston works a valve *v*, which controls the steam supply. The spring *f* insures the return of the piston, the movements of which are recorded by the indicator I, which thus acts as a thermometer. Nauman's thermostat consists essentially of a double-walled bath, the space between the two walls being filled with a liquid boiling at a higher temperature than that required in the

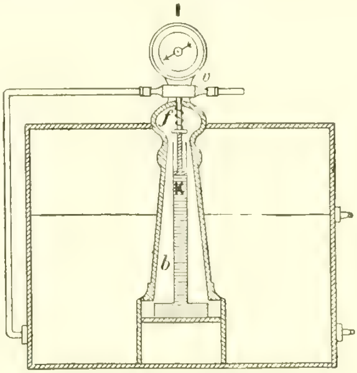


Fig. 12.

bath. In this liquid is immersed a vessel filled with mercury, from which a small-bore tube *b* passes outside the bath (fig. 13). The end of the tube *b* dips into the vessel *c*, which is suspended on one arm of a ring-formed balance beam *d*. The expansion or contraction of the mercury in the reservoir expels mercury into or takes it from the vessel *c* by means of the tube *b*. The consequent movements of the balance-arm control the size of a petroleum flame used for heating the bath, by means of a lever *n* (D. P. J. 226, 276).

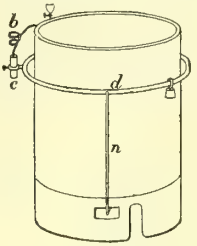


Fig. 13.

D'Arsonval constructed a very delicate thermostat (fig. 14) by surrounding his oven with a chamber completely filled with water, which is introduced through an opening *v*, closed by a screw or by a cork through which a thermometer passes. Connected with this water chamber is the side tube o, closed by a caoutchouc membrane. Near to the centre of the surface of the membrane the gas-supply tube terminates, in a small metallic valve-box, from which the gas is led off to the burner by the tube *d*. The expansion or contraction of the large volume of water in the outer chamber causes the caoutchouc membrane to lessen or increase the distance between the supply tube and its own surface, thus forming a very sensitive valve, which controls the supply of gas to the burner. This regulator is said to keep the temperature constant to $\frac{1}{200}^\circ$ (J. Ph. [4] 26 474).

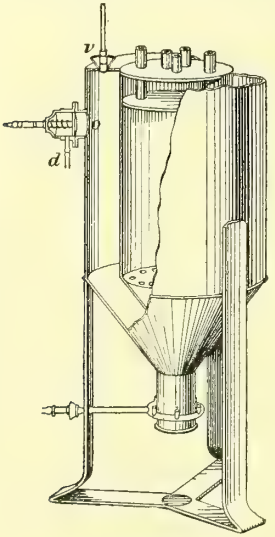


Fig. 14.

To maintain constant higher temperatures than can be employed with water, D'Arsonval substitutes a brass tube (fig. 15), containing petroleum or glycerol, for the surrounding water chamber. The membrane is replaced by a corrugated metallic plate such as would be used in an aneroid barometer; *b* is a leaden tube prolonging the brass tube, it is hermetically closed after charging the tube. The chamber at the back of the aneroid plate communicates with the main tube by two small tubes *m* and *n*.

Several other forms of this regulator, retaining the same kind of valve, have been constructed. The valve itself has been mounted separately on a stand, and provided with a funnel and stopcock to adjust the amount of liquid in the connected reservoir and the lower part of the valve, and with a by-pass to insure that the flame be never quite extinguished. The same type of valve has also been adapted to the regulation of the flow of a cooling mixture, used for obtaining temperatures below that of the surrounding air.

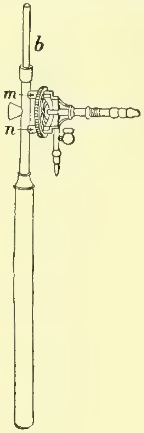


Fig. 15.

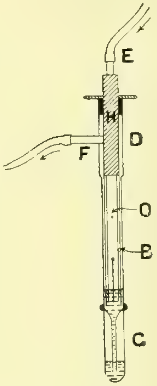


Fig. 16.

For an early form of regulator belonging to this class, devised by Lemares in 1835, *v.* D. P. J. 56, 474. In the thermostatic battery by Dibdin and Smith, in use at the metropolitan gas stations, large mercurial thermometers are employed. The tubes by which they communicate with the supply tube are provided with stopcocks, so that any one or more of them may be thrown out of action. They control the gas supply to the boiler connected with the hot-water pipes.

(*b*) *Gas thermometer regulators.*

1. *Acting on the gas supply through a liquid piston.* A thermostat on this principle was devised by Kemp (D. P. J. 117, 352) and improved by Westly.

Muencke has converted the Gerhardt-Reichert thermostat into an air-thermometer instrument (Fr. 15, 321). The form of this instrument made by Wiessneg has an independent continuous gas supply.

Cresti's regulator differs from Muencke's in form only (Gazz. Chim. 1878; B. 1878, 2030).

Bunsen's thermostat is a modification of Kemp's. The gas supply and exit tubes are arranged as shown in fig. 16; the supply tube E passes through a brass cylinder H, which screws into the loose brass cap D. At its lower end is a slit, and it is provided with a minute orifice at O; the exit tube F is joined on to the side of the cylinder H, the latter being continued by the glass tube B to the same depth as the supply tube. The cap is fitted on a brass tube supplied with a slit in which the tube F can slide. A glass cylinder closed at the lower end continues this brass tube. In the lower part of this glass vessel is a glass air-chamber opening downwards and closed by the mercury contained in the cylinder; this air-chamber preferably takes the form shown at G. The expansion of air in the chamber causes the mercury to rise in the cylinder, and thus partially closes the slit; the position of the slit is regulated by the screw cap till the required temperature is attained. The minute orifice O insures that the gas supply should never be completely cut off (D. P. J. 143, 342).

An improved Bunsen-Kemp regulator by Schorer separates the air-thermometer reservoir from the valve, as shown in fig. 17. This device enables the instrument to be used for high temperatures (Fr. 9, 213).

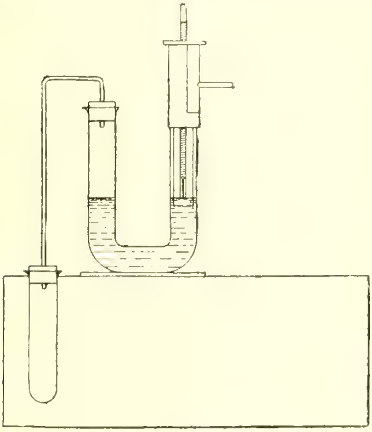


Fig. 17.

J. Martenson's regulator is on the same principle (C. C. 1872, 513).

Bunsen's low-temperature regulator has a larger air chamber, and is provided with a side tube and stopcock, by means of which the amount of mercury present can be readily altered (Desaga's Catalogue). Pontallie divides the gas supply after passage through a Bunsen's regulator, using one part to heat the regulator only, the remainder heating the bath. As these quantities are in exact and determined proportion, the temperature of the bath is maintained constant when that of the regulator does not vary.

Guthrie's thermostat consists of a U-tube, into which is fused a Kemp tube, provided with a side arm fused on at an acute angle, and bent parallel to the arms of the U-tube. The expansion of the air in the bulb causes the mercury to partially interrupt the communication between the two arms of the U-tube, which serve as supply and exit tubes respectively. Adjustment of the mercury level is made by means of a piston in the side arm (P. M. [4] 36, 30).

D'Arsonval adapted his thermostat for use at temperatures between 150° and 1,200°C. by substituting an air reservoir for the petroleum reservoir employed at lower temperatures. The reservoir was made of glass or porcelain. The aneroid valve was at the same time furnished with a lever-arm and weight P, by means of which the pressure on the lower surface of the aneroid plate could be more or less compensated, and the amount of gas supplied altered at will (fig. 18; J. Ph. [4] 26, 474).

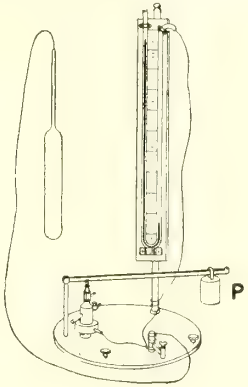


Fig. 18.

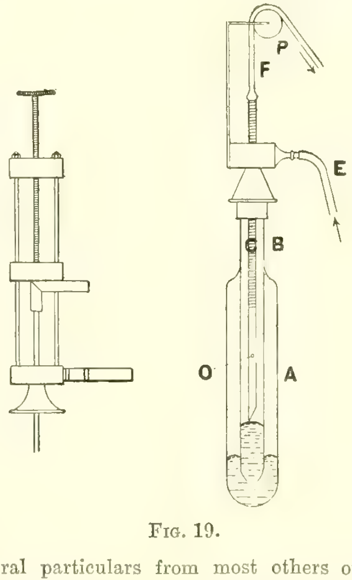


Fig. 19.

The form of air-thermometer thermostat invented by E. H. von Baumhauer differs in several particulars from most others of this type (see fig. 19). A is the air-vessel fixed on to the tube B, which is carried nearly to the bottom of A, and there ends in a somewhat contracted opening. The tube B is closed above by a metallic stuffing-box, through which slides a graduated tube C, cut off at an angle at its lower extremity. The caoutchouc connecting tube F, joined to the tube C, works over a pulley P, supported by the stuffing box. Gas enters the instrument at the side tube E, passes down B, and through C and F to the burner. Mercury is placed in the tube A in sufficient quantity to seal off the air space at the highest temperature for which the instrument is required to be used. Expansion of the air in A forces mercury up B, and cuts off the gas supply in the usual manner. Complete extinction of the flame is prevented by a small supply of gas passing through the hole O.

An arrangement is also figured by means of which the graduated tube C can be screwed up and down as may be required for adjustment of the flame (Fr. 24, 42).

Other forms are due to Clowes (C. J. 24, 639, 1871), Rügheimer (B. 20, 1, 1280, 1887), and Kalecsinsky (Fr. 25, 190) and Tollens.

2. *Acting through electrical arrangements.* Pfaundler devised the apparatus illustrated by fig. 20. V is an air reservoir weighted with mercury and sunk in the bath, of which the temperature is required to be constant. This is connected with the wider limb of the manometer *m m* containing mercury. The mercury in this limb is permanently connected through the wire *s g n*, and the electro-magnet of the valve with one pole of the battery K.

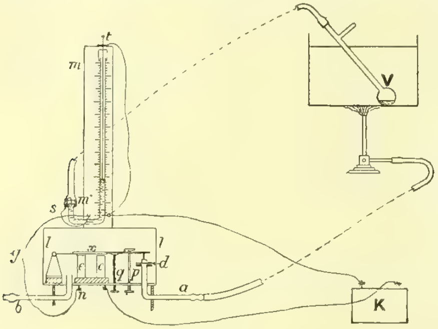


FIG. 20.

The mercury in the narrow limb is connected with the other pole of the battery, whenever by the expansion of the air in V it may be forced sufficiently high to form contact with the adjustable wire *t*. The valve-box is an hermetically closed vessel *l*, into which the gas-supply tube *b* opens, and from which the gas is conducted to the burner through the tube *a*. The flow of gas through *a* is controlled by a plate valve *d*, carried by the armature *x* of an electro-magnet *e e*. The play of the valve is regulated by the screw-stops *p* and *q*. When the required temperature is reached, the current closes the valve, which reopens as soon as contact is broken in the manometer. The regulating stop *q* can be so set that the valve never quite closes, and hence the flame is always supplied with sufficient gas to prevent extinction (Carl's Rep. 18, 443). *V.* also Martenson, C. C. 1872, 513.

3. *Acting through mechanical arrangements.* Jeannel's thermostat (fig. 21) is an air-thermometer thermostat in which the air reservoir consists of a metallic vessel of 300–400 c.c. capacity. This is connected with one limb of a U-tube containing glycerol. In the other limb a float G carries a steel needle working loosely in a fine caoutchouc tube O. By a rise of the liquid in F, the float, guided by the steel needle, brings the flat upper surface of the sealing-wax H, in which the needle is mounted, near to the mouth of the tube O, thus forming a valve controlling the current of gas from the supply tube J to the exit tube P, of which O is a continuation. The pressure of the air in A is modified at pleasure by means of the caoutchouc pump S, with which connection is made through the tap R on a side tube (A. Ch. [4] 25, 386). Bendix and Lohse (Germ. Pat. 14,242, 1880; B. 14, 2,608*b*), and Bechem (Germ. Pat. 18,077, 1881; B. 15, 1,226*a*) have also devised self-acting thermo-regulators of this type.

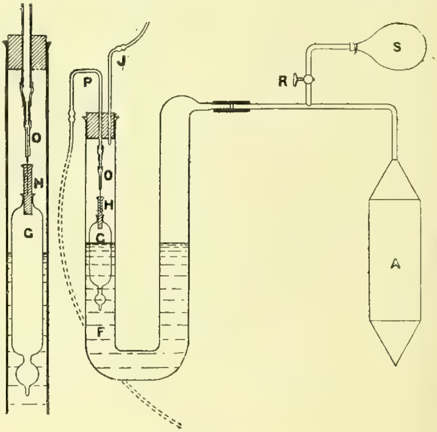


FIG. 21.

An apparatus arranged by W. T. Richmond presents some novel features. This thermostat consists of an air-thermometer, immersed in the bath of which the temperature is required to be kept constant, acting through a mercury column on an electric valve of peculiar con·

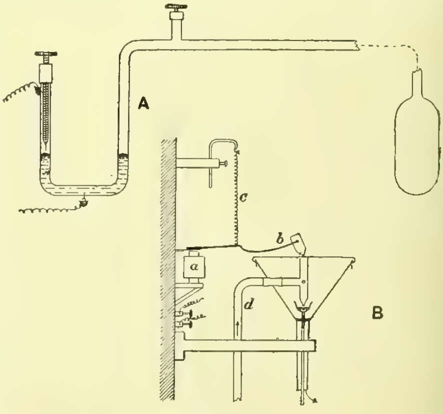


FIG. 22.

truction, by the completion or interruption of n electric circuit. The mercury make and reak is shown at A, fig. 22, one pole being in onnection with the mercury at the bend of the U-tube, by means of a platinum wire fused hrough the glass and dipping into a mercury up outside to diminish the chance of breakage, he other connected with a straight platinum vire fused into a thick-walled glass tube passing lown the outer limb of the U-tube. This limb s provided with a screw-cap, which may be closed as-tight; the instrument is then independent of tmospheric variations of pressure and temperaure; it is to reduce the volume of the air menable to the latter irregularity that the thick lass tube is placed round the platinum wire. There is a regulator cap and screw attached etween the U-tube and the bulb, which is screwed down when the required temperature s reached; any further expansion of air in the bulb forces the mercury up the outer limb, completes the circuit, and thus calls the valve into play.

The valve is shown at B, fig. 22. An electromagnet *a* depresses a valve when the current is made; when the current is broken the arm *b* is raised by the spring *c*. The valve itself consists of a T-piece, supported by one arm on the centre of a sheet of india-rubber stretched over the mouth of a funnel. The leg of the T-piece is connected with a flexible caoutchouc tube passing gas-tight through a hole drilled in the side of the funnel, and joining the gas-supply pipe *d*. The other arm of the T-piece opens just above the surface of some mercury in a small cup supported on a screwed rod passing loosely through the neck of the funnel, and working in the loose nut placed in the angle of the funnel; its height can hence be adjusted as required. The gas passes through the leg and lower arm of the T-piece, and is carried off to the flame through the tube of the funnel. When the temperature passes the assigned upper limit the current is made, *b* is depressed by the magnet *a*, the T-piece is forced down on to the surface of the mercury, and thus the gas supply is cut off. A small hole drilled in the T-piece allows a sufficiency of gas to pass to prevent extinction of the flame (Am. 5, 287).

(*c*) *Vapour-tension thermometers.*

1. *Air and vapour.* Andreæ's thermo-regulator is a Kemp thermostat in which the expansion of the air in the reservoir is increased by the addition of a small quantity of some readily volatile liquid. Such liquids as ether, alcohol, acetone, petroleum ethers, and water may be employed for the purpose. Ether is particularly suitable, on account of the rapid increase of its vapour tension with increase of temperature. A thermostat of this form will maintain the temperature of a water-bath constant within 0·04–0·05°C. (W. 4, 614).

To Lothar Meyer is also due the application of the same principle (B. 16, 1088).

Benoit's thermo-regulator has the thermometer reservoir separated from the valve, connection being made by means of a caoutchouc tube containing mercury.

The reservoir consists of a thin tube, drawn out at one end for convenience in filling, which contains a small quantity of air, and a few drops of some volatile liquid; the remainder of the space in the tube is occupied by mercury in connection with the mercury in the valve by means of the caoutchouc tube. The valve differs somewhat from the ordinary form. It is provided with a side tube A (fig. 23), by which a small amount of gas can directly pass from the supply tube *x* to the burner tube *y*. Mercury can be added by means of the side tube B, or withdrawn from the cock C to adjust the level within the valve. The whole is mounted upon a sliding board, fixed by the clamp-screw M, at any convenient height (Wied. Beibl. 4, 296; Guillaume's Thermométrie, p. 130).

2. *Vapour in contact with its own liquid only.* The instrument devised in 1886 by G. W. A. Kahlbaum belongs to this class. There is the usual mercury valve, the supply tube being bevelled off at the open end at an angle, and having a small hole opposite the exit tube to provide against total extinction of the flame. It may be adjusted according to the temperature required by the rack and pinion shown (fig. 24). The other limb of the U-tube contains a liquid of boiling-point just below the temperature required in the bath or oven. For facility in changing the liquid, this end of the tube is closed by a tightly-fitting cork held in place by a clamp working against an india-rubber seat fixed on the collar of the glass tube.

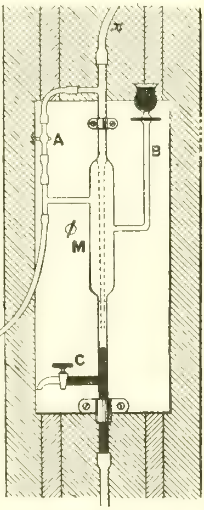


FIG. 23.

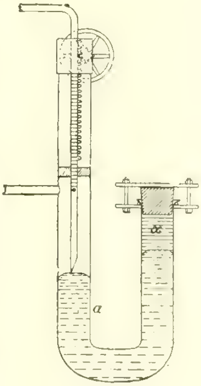


FIG. 24.

The temperature rises just above the boiling-point of the liquid *x*, a portion of this volatilises, and mercury is forced up the limb *a*; the pressure on the liquid being now greater, its boiling-point is raised, and the temperature must increase for further volatilisation to occur. Owing to the rise of mercury in *a*, the gas supply is diminished, and hence the temperature falls. Consequent on the fall of temperature, a portion of the vapour condenses, the valve is opened to a greater extent, and the temperature again rises. These actions soon reach a point of equilibrium, and a constant temperature is then maintained (B. 19, 2860*b*).

(*d*) *Thermostats depending upon the differential expansion of solid bodies.* Bonnemain (D. P. J. 16, 285) and Ure (D. P. J. 42, 173) have devised regulators depending upon the expansion of simple or compound metallic bars.

Hipp's thermostat is only available for temperatures between 30° and 40°C (see fig. 25). It consists of a copper vessel K, surmounted by a wooden box C, having glass front and back. A system of tubes on the walls of the oven communicate with the vessel K, and serve for the circulation of the water heated in that vessel. They are provided with openings for filling in water, and to serve as escape vents in case the water may be accidentally boiled. The temperature is controlled by a regulator consisting of a bent compound metallic bar fixed upon the back wall of the oven at A; the free end B is connected by a copper wire with the lever *k* working a conical valve *v*; *z* is a regulating screw, by means of which any desired initial opening of the valve may be obtained; *s* is the gas-supply tube, and *t* draws off gas for the burner from the valve-box R (D. P. J. 191, 366).

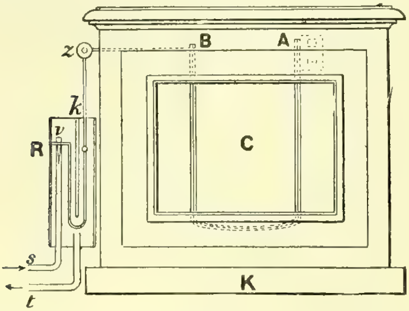


FIG. 25.

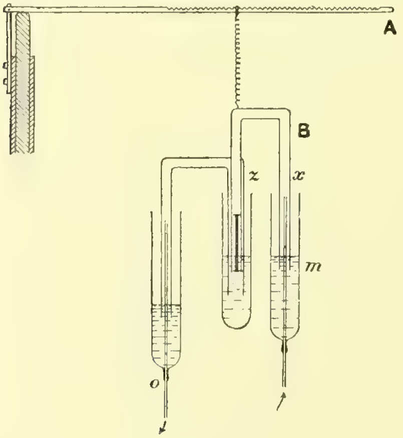


FIG. 26.

Lothar Meyer in 1884 devised a sensitive temperature regulator on this principle (fig. 26). It consists of a long brass tube placed vertically in the bath, and closed at its lower extremity; in this tube a slightly longer glass rod is placed. The tube supports a rod carrying a movable lever-arm A, from which depends a floating valve B. The valve may be placed at varying distances along the lever-arm A, so that the difference between the expansions of the brass tube and glass rod may be magnified to a greater or less extent in the amount of movement imparted to the valve. The supply tube is a narrow-bore tube passing up the arm *x* of the valve working in the glycerine seal tube *m*. The supply tube and seal may be adjusted to any required height. A precisely similar arrangement allows of the drawing off through *o* of the gas for the burner. The valve *z* is essentially a Bunsen mercury-and-slit-tube valve. The mercury vessel is adjustable to any required height (B. 17, 478*a*).

L. von Babo arranged a gas regulator, in which the control valve depends for its action upon the unequal expansion of glass and copper. In fig. 27, A is a copper tube, B a glass rod. The valve *x*, which regulates the flow of gas from the supply G to the burner tube E, is fixed in position by the glass rod B, against which it is pressed by a spiral spring C. The screw D serves to adjust the position of the glass rod, and renders it possible to obtain a greater or smaller supply of gas at will. As the temperature rises, the expansion of the copper tube being greater than that of the glass rod, the valve *x* is pressed by the spring C nearer to its seat, and so there is less gas supplied; the temperature then falls, and the valve partially re-opens, and so on (B. 13, 1221*a*).

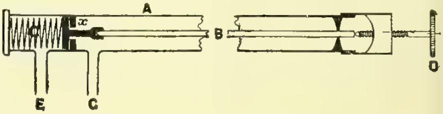


FIG. 27.

Kohlrausch employed a Breguet's metallic thermometer to make and break an electric current, which heated a fine platinum wire (P. 125, 626).

Rieth's instrument consisted of a compound metallic bar working a cone valve, supplied with a regulator screw (C. C. 1871, 615).

(*e*) *Other mechanical regulators* have been devised by J. W. Eichler and H. Hartig (Germ. Pat. 5,492, 6, Nov. 1878), and by Appold, whose instrument was a balance regulator (Pr. 15, 144, 1866).

The invention of G. J. Meurlin (Germ. Pat. 4,703, 27, Aug. 1878) consists of a self-regulating cone valve to control the pressure of a gas supply, and hence the temperature of a space heated by the flame. The pressure of the gas in the chamber *a* raises the cone *b* (fig. 28), partially closing the hole in the plate *x*, and thus restricting the current. The hole in the summit of the cone *b* prevents extinction of the flame.

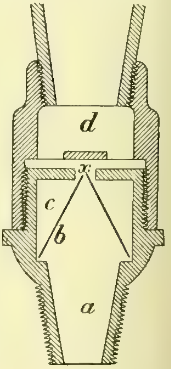


FIG. 28.

Detailed information concerning many of these forms of apparatus is given by J. T. Brown, Temperature Regulators; Laspeyres, P. 152, 132; and H. Hammerl, Carl's Rep. 18, 1882.

W. T.

THIET-SIE. A resinous substance used as a varnish by the Burmese. It exudes from a tree in form of a light-brown, very viscid liquid of the consistence of treacle, but on exposure to the air for a few minutes becomes quite black and hard on the surface. The same change takes place instantly in contact with caustic potash. The resin spread in a thin layer on wood or other solid bodies quickly forms a hard deep-black coating of great brilliancy. On digesting the unaltered substance with alcohol of 80 per cent. at a gentle heat, the greater part gradually dissolves; and on decanting the clear liquid from the insoluble residue, and distilling off the alcohol, there remains a very tenacious gummy residue of a rich-brown colour, which undergoes no change of colour on exposure to the air, but very slowly hardens. In contact with caustic potash, however, it blackens like the original substance.

The residue, insoluble in alcohol, dissolves for the most part in ordinary ether, forming a dark-brown solution, and leaving a light-brown solid resin. The ethereal solution, when evaporated, leaves a residue which, on exposure to the air, instantly becomes quite black, and after a short time nearly solid. This, then, is the portion of the original substance to which the property of blackening on exposure to the air is due.

The solid resin, insoluble in alcohol and ether, which forms but a small part of the original substance, is quite unalterable in the air. When heated with nitric acid, it yields a crystalline sublimable acid, exhibiting the characters of succinic acid (H. Watts).

THIOCRESOLS *v.* PHENOL AND ITS HOMOLOGUES.

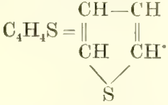
THIOCYANATES *v.* CYANIDES.

THIOFLAVINES. When *p*-toluidine is heated with sulphur it yields bases containing sulphur, and these, when converted into their methyl, ethyl, or benzyl derivatives, give yellow colouring matters. The following example illustrates the method employed: 24 kilos. of the sulphur base from *p*-toluidine are heated in an autoclave with 30 kilos. of methyl alcohol and 12 kilos. of hydrochloric acid of 1·16 sp.gr. for 12 hours to 170°; the whole is then boiled with water, when part of the product dissolves, and after filtration is precipitated by the addition of salt. This forms a basic colouring matter which dyes cotton, mordanted with tannin and tartar-emetic, a bright yellow. It belongs to a group of colouring matters to which the name Thioflavine T is given. 25 kilos. of the product, insoluble in water, are dissolved in 70 kilos. of sulphuric acid, 10–12 kilos. of sulphuric acid containing 60 per cent. SO_3 are added, and the whole raised to 80°. When the sulphonation is complete, the melt is poured into cold water, which precipitates the sulphonic acid. This is dissolved in an alkali, and precipitated with salt and dried. The new colouring matter belongs to the group Thioflavine S, and dyes unmordanted cotton a bright yellow from an alkaline bath. Dyestuffs belonging to the Thioflavine S group may also be obtained by alkylating the sulphonic acids of the sulphur bases from *p*-toluidine (S. C. I. 8, 771).

THIOLINE *v.* ABIETENE.

THIONINE *v.* METHYLENE BLUE.

THIOPHEN. *Thiofurfuran*



Discovered by Victor Meyer in coal-tar benzene, which contains about 0·5 per cent. of thiophen (B. 16, 1465; S. C. I. 1883, 325). In order to extract the thiophen, a large quantity of the best commercial benzene was shaken for some hours with one-tenth of its volume of concentrated sulphuric acid, the black acid layer separated, diluted with water, and converted into the lead salt of the sulphonic acid thus obtained. This lead thiophen-sulphonate, which was contaminated with lead benzene-sulphonate, was dried, mixed with one-fourth of its weight of ammonium chloride, and distilled. The sulphonic acid was thus hydrolysed, and an oil passed over which was purified by shaking with caustic alkali to remove mercaptans, dried over calcium chloride and rectified. The rectified oil boils at 84°.

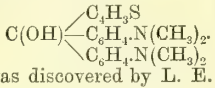
K. E. Schulze (B. 18, 497) recommends that the thiophen-sulphonic acid, after diluting the crude acid with water, should be hydrolysed by steam-distillation.

Thiophen has been artificially prepared by numerous methods: amongst others by passing ethylene or acetylene into boiling sulphur (Victor Meyer a. Sandmeyer, B. 16, 2176); by heating succinic anhydride with phosphorus pentasulphide, or better, sodium succinate with phosphorus trisulphide (Volhard a. Erdmann, B. 18, 454; Friedburg, A. C. J. 12, 83, 90; S. C. I. 9, 1062); and in the same way from erythrol and phosphorus pentasulphide (Paal a. Tafel, B. 18, 688).

Liquid, with a faint smell. Boils at 84° (cor.), sp.gr. at 0° = 1·08844. Gives with isatin and sulphuric acid a blue colouring matter—indophenin $C_{12}H_7NOS$ (test for thiophen in benzene). Thiophen gives similar coloured condensation products with all compounds containing the group CO.CO.

Both in its physical properties and in its chemical reactions, thiophen closely resembles benzene. Benzene boils at 80°, thiophen at 84°. The halogens, nitric acid, and sulphuric acid react with thiophen, yielding substitution products corresponding with those of benzene, excepting that thiophen, owing to its unsymmetrical constitution, forms *two* series of mono-substitution compounds—α-compounds, in which a hydrogen atom adjacent to sulphur is replaced, and β-compounds, in which the substitution takes place with a hydrogen atom in the meta- or β-position to sulphur. By treating a mixture of iodo-thiophen and methyliodide with sodium, methylthiophen (thiotolene) can be obtained. Both the methylthiophens occur in coal-tar. Methylthiophen, on oxidation with potassium permanganate, is converted into thiophen-carboxylic acid—an analogue of benzoic acid. Nitrothiophen, like nitrobenzene, yields, with reducing agents, the corresponding amido- compound. Dithiënyl $(C_4H_3S)_2$ is formed when the vapour of thiophen is passed through a red-hot tube, just as diphenyl $(C_6H_5)_2$ is formed under these conditions from benzene.

Thiophen green



$$C(OH)\begin{cases}C_4H_3S\\ C_6H_4.N(CH_3)_2.\\ C_6H_4.N(CH_3)_2\end{cases}$$

This compound, which was discovered by L. E. Levi (B. 20, 513; S. C. I. 1887, 505), is an analogue of malachite green. The leuco-base $CH(C_4H_3S)[C_6H_4.N(CH_3)_2]_2$ is first prepared by heating one part of thiophenaldehyde $C_4H_3S.CHO$, two parts of dimethylaniline with a little alcohol, and three to four parts of zinc chloride together for six hours, adding the zinc chloride gradually, and, if the mass becomes thick, diluting slightly with water. The product is made alkaline with caustic soda, steam-distilled, extracted with ether, and the crystalline residue which is left on evaporating the ether recrystallised from alcohol. This crystalline leuco- base is then oxidised with manganese dioxide and dilute sulphuric acid, when it yields thiophen green. The colouring matter is extracted with hot water, filtered from manganese dioxide, precipitated with ammonium chloride and ammonia, and extracted with ether. It is, as represented by the formula, the carbinol corresponding with the leuco- base. Like malachite green, it forms a double salt with zinc chloride. It dyes silk and wool a shade very much like that of malachite green, but somewhat yellower.

W. Krause (Internat. Monatschr. f. Anat. u. Physiol. 4, 2; S. C. I. 1887, 507) recommends the use of the zinc double salt of thiophen green for staining sections, especially as a complementary colour to carmine. It dissolves readily in water, alcohol, and chloroform, but is insoluble in benzene. F. R. J.

THIOPHENOL *v.* Phenol and its homologues.

THIORESORCINOL *v.* Phenol and its homologues.

THIOSTANNIC ACID *v.* Tin salts and oxides.

THORITE *v.* Thorium; also Cerium metals.

THORIUM. Sym., Th. At. wt. 231·87 (Krüss a. Nilson). Thorium occurs in *thorite*, *orangeite*, *monazite*, *pyrochlor*, *euxenite*, and other minerals containing metals of the cerium group.

It has been obtained as a grey powder of iron-grey lustre when burnished, and sp.gr. 10·968 (Nilson), and in minute, brittle, almost infusible crystals of the cubical system of sp.gr. 11·23 (Nilson). Thorium is unalterable in air below 120°, but burns brilliantly below a red heat, with formation of the white oxide. It is without action on water, and dissolves slowly in dilute sulphuric and hydrochloric acids, more rapidly in concentrated hydrochloric acid, but is insoluble in alkalis. It combines directly with sulphur.

Thorium belongs to the group of metals containing tin, titanium, and zirconium. It forms a white oxide ThO_2, which has been used with zirconia in the cap of Welsbach's incandescent gas-burner (*v.* Zirconium). According to Clève, a higher oxide Th_2O_7 also exists. A disulphide, tetrachloride, tetrafluoride, and sulphate and other salts are also known.

THORN APPLE *v.* Datura.

THSING-HOA-LIAO. A Chinese name for a cobaltiferous aluminic silicate used in the manufacture of porcelain; also applied to a cobaltiferous manganese ore used for producing a blue colour on porcelain.

THULIUM *v.* Cerium metals.

THYME CAMPHOR *v.* Camphor.

THYME OIL *v.* Oils, essential.

THYMOL *v.* Camphors; also Phenol and its homologues.

TIERS ARGENT *v.* Aluminium.

TIGER EYE *v.* Crocidolite.

TIGLIC ALDEHYDE, TIGLIC ANHYDRIDE *v. Guaiacum*, art. Resins.

TIL or **TEEL OIL** *v.* Sesamé oil.

TILE ORE. An earthy variety of native cuprous oxide.

TIMA. A medicinal preparation imported from Tampico as a remedy for phthisis. Is prepared as a syrup by boiling the fruit of *Crescentia edulis* with sugar, and mixing the product with almond oil (Ar. Ph. [3] 107, 375).

TIMBO. The name of a narcotic medicine, the root rind of the *Conchocarpus Peckolti.* The rind appears in the form of tubes or rolls, is bright reddish-brown on the outside and yellowish on the inside. The outer and middle rind break off short, but the inner rind has a long fibrous fracture and the interior colour is whitish. It possesses a weak aromatic taste somewhat like cascarilla bark, but has no special odour. A cross-section shows an interrupted yellow zone near the outer side, whilst the inner rind is faintly streaked in radiating lines. Some of the cells contain crystals of calcium oxalate (Chem. Zeit. 11, 315; S. C. I. 6, 560.

TIN. Sym., Sn. At. wt. 117·35. Tin was known and prized in the earliest historic ages, for it is mentioned without comment as one of the common metals in the days of Moses (Numbers xxxi. 22), and was an important commodity in the fair at Tyre; numerous bronze instruments of very early date have also been discovered in Assyria, and particularly by Layard in the ruins of Nineveh. Many of these bronzes are now preserved in the British Museum. The tin so employed was obtained by the Phœnicians from Cornwall and the Scilly Isles in this country, and from the mountains of Spain, and there is no evidence of the occurrence of tin in those countries in which, in ancient times, the metal was most largely used. Pliny appears to have been familiar with tin, and states that it occurs in grains, in alluvial soil, from which it is obtained by washing. These grains, he further states, are black, and their metallic character can only be recognised by their great weight. Though tin was regarded by the ancients as one of the baser metals, its cost was greater in the days of Homer and Pliny than at present, for in the days of the latter of these writers an avoirdupois pound of tin cost 8*s.* 7¼*d.* sterling, or about 9½ times its present value. The uses of tin among the Romans were similar in many respects to those of the present day. It was chiefly employed in the form of an alloy with copper, on account of the hardness imparted to the alloy by a comparatively small proportion of tin, and some of the very earliest known bronzes agree closely in composition with those used for similar purposes at the present day.

Tin was also used with lead by the Romans for the production of solder, and for tinning the inside of copper and brass vessels, in which art the Roman workmen appear to have attained considerable skill. Alloys containing more tin, corresponding somewhat to the modern *speculum metal*, were used by the ancients for mirrors, but the art of tinning iron does not appear to have been discovered till a much later date. For further details *v.* Thomson's Hist. of Chem., i. 69; also art. TIN in Chemistry Applied to Arts and Manufactures.

Occurrence of tin. Tin occurs in comparatively few localities, never in the native state, and in but few forms of chemical combination. The most important ore is *tinstone* or *cassiterite*, the dioxide of tin (SnO_2), which is met with in two principal forms, crystallised and massive. The crystals are of the regular prismatic or tetragonal system, isomorphous with those of rutile, and are frequently well formed and of tolerable size. Tinstone in the usual or massive form is a dark reddish-brown or slaty-coloured very heavy mineral, which occurs in Cornwall in veins which usually run nearly east and west, and in which the tin ore is associated with arsenical pyrites, sulphide of copper, wolfram, and a great variety of other minerals. Tin usually occurs in plutonic or metamorphic rocks, such as granite, felspar, porphyry, or clay slate, but by the action of denudation on these older rocks grains of tinstone are frequently met with in the neighbouring alluvial deposits, and this variety of ore, which is of special purity and now almost entirely exhausted in this country, is known as 'stream tin.' The metal also occurs in small quantities as *tin pyrites* (SnS_2). The largest quantities of tin are now produced in the island of Banca ('Straits tin') and in Britain. Smaller though considerable quantities are met with in Germany, Austria, Siberia, New South Wales, and Bolivia. For some years past reports have been circulated which state that immense deposits of tin ore have been discovered in the United States, in Dakota, and elsewhere, but up to the present (January 1892) only experimental work has been carried on in the districts mentioned, and no influence has yet been produced upon the world's supply of tin (*v. Iron*, 37, 512).

Production of tin. The metallurgy of tin is in its main features simple, but the mechanical preparation of the ore involves more skill and labour than is the case with any of the other common metals. So much, in fact, is this true that success in the extraction of tin frequently depends more upon the captain of the mine, who superintends the dressing of the ores, than upon the smelter. On account of the high price of tin, which for some time recently has averaged nearly 100*l.* per ton, and the relatively high density of tinstone, it is found practicable to work ores which in the first place contain comparatively little tin, ores which contain only 0·5 per cent. of tinstone being sometimes profitably worked. The principle adopted in the mechanical separation of tinstone is very simply illustrated in the operation of 'vanning,' which is frequently used in Cornwall and elsewhere as an approximate test of the richness of an ore. A quantity of the crushed material is placed in a miner's shovel of special shape, known as a vanning shovel, water is added, and then by means of a circular motion which is imparted to the shovel by the hands, aided by a peculiar jerk of the wrist, the ore is ultimately almost completely separated from the earthy matter, and can be dried and weighed. On the large scale the ore is first picked and assorted, and then broken by suitable rolls or stone crushers. The roughly-powdered ore is carefully assorted, and then fed into a mill containing a battery of stamps, of which there are many varieties in use. Each stamp weighs some 3 cwt., the face of the stamp being either steel or chilled cast iron. By means of suitable cams on a revolving wheel the stamp is raised at regular intervals, and allowed to fall upon the ore which is contained in the box or coffer of the stamp. A supply of water flows through the boxes and escapes through perforations, carrying away the finely-crushed ore, while the larger pieces remain in the box to be further crushed by the stamp. The finely-powdered ore now passes to some form of buddle, which more or less completely separates the earthy matter. Probably the simplest form of such apparatus, of which there is endless variety, is the inclined plane with ridges or 'riffles' placed at right angles to its length. On such a plane the heavier particles naturally remain, the richer fragments being deposited principally at the upper part of the buddle, while the earthy matter, with some ore, passes away. But such a simple form of buddle is now seldom used, and a considerable number of improvements have been from time to time proposed. Thus the inclined plane is made movable, and either a jerking or a rocking motion is imparted to it, and this is found to give better results than the fixed form. But buddles of a circular shape have met with considerable favour in recent years, one form (Borlase's) being a circular concave buddle fed from the outside and discharging the slimes from the middle; but the variety generally preferred in Cornwall is that of a very flat cone, the water and ore being distributed either by a revolving spout, near the apex of the cone, or by means of a smaller and more acute distributing cone. The waste liquid from the buddle is led into a succession of tanks or pools, where it is allowed to settle in order to recover the finer portion of the ore, which would otherwise be lost, and the slimes thus obtained are worked over again from time to time.

In dressing tin ores it is important that they should not be too finely crushed, or the gangue will be removed with greater difficulty. The ore should be as far as possible separated into parcels, the fragments in each being of uniform size, and the method of treatment is varied with the fineness of the material; in no case should the ore be crushed more than is necessary to separate the matrix. These facts form the basis of all successful ore dressing.

Reduction of tin. From the point of view of the tin smelter, ores of tin may be divided into two classes, first those of tolerable purity, which may be directly smelted in the furnace, and secondly a less important class of ores, which, from the fact that they contain notable proportions of copper, arsenic, sulphur, or wolfram, require to be further treated, after dressing, before smelting. Ores which contain arsenic or sulphur are roasted in large calciners at a low temperature, and rabbled at intervals until the greater part of the sulphur and arsenic has been removed; the mass is then withdrawn, and, after being exposed for some time to the action of the atmosphere, is washed, to remove the oxide of iron and other lighter matters from the heavy oxide of tin. Ores which contain much wolfram are heated with sulphate or carbonate of sodium in a reverberatory furnace, by which soluble sodium tungstate is produced, and can be removed by washing from the unaltered oxide of tin. That this process (Oxland's) is not now carried on to any considerable extent may be assumed from the fact that the 'Mineral Statistics' show in 1886 a production of only 11 tons of sodium tungstate, and this amount fell in the following year to 1 ton. The ore having been purified by one or other of these processes is ready for smelting in the ordinary way. The reduction of the metal from the ore is always accomplished by heating with carbon, which operation may be performed either in a reverberatory furnace, as is the custom in this country, or in small blast furnaces such as are used to a limited extent in Germany.

Tin smelting in England. The furnace employed for the smelting of tin in this country, and in fact pretty generally elsewhere, is a reverberatory, with a fireplace at one end and a stack at the other. At the front is a single working door, while at the back is a tapping hole which is closed during the smelting, but which when the operation is concluded serves to convey the metal into a 'float' or circular iron pot lined with clay. The bed of the furnace is about 18 feet long by 9 feet broad, and slopes to the tapping hole. The fireplace is about 2 feet broad, and the firebridge is of firebrick and some 14 inches high. The roof is low, and slopes uniformly from the firebridge to the stack.

The charge of ore, which weighs 20 to 25 cwts., is mixed with rather less than one-fifth of its weight of anthracite powder, and spread uniformly over the furnace bottom. If the ore is refractory, a little fluorspar or lime is added as a flux. The door is then closed and luted up, and the temperature gradually raised for five to six hours, when the door is opened, the mass rabbled, and a quantity of powdered anthracite or 'culm' is thrown on the surface of the charge. After heating for about another hour, and a further rabbling, the metal is tapped. Part of the slag produced is thick and is raked out of the furnace, while the remainder is more fluid, flowing out with the metal, and is called 'glass' by the smelter. The slag consists essentially of ferrous silicate, and as it frequently contains a considerable amount of tin it is melted again when the furnace is at liberty.

Small blast furnaces, which were previously used in this country, have survived longer in Germany, and are also employed by the natives of India. The waste of metal is much greater than in the reverberatory, while the cost of fuel (charcoal) is also greater than in England, but the tin obtained is stated to be of excellent quality.

Refining. The refining process consists of two parts, a preliminary liquation, and the refining proper. The liquation is conducted in a furnace of similar shape to the reverberatory above described, and about 18 tons is operated upon at once. The temperature is carefully regulated so as to just melt the purer tin, which gradually flows away into a separate pot or 'kettle,' while the impurities, consisting of iron, arsenic, copper, sulphur, and traces of many other elements, together with some 20 p.c. of tin, remain in the form of a hard, brittle, white, semi-metallic mass known as *hard-head.* The purer metal which has collected in the kettle (which is heated by a small separate fire) is now refined by plunging billets of green wood under the surface of the melted tin. A quantity of gas is evolved from the wood, and violently agitates the metal, gradually separating a scum which contains the impurities originally present in the crude tin. The same result is sometimes attained by 'tossing' the melted metal in ladles from a height of several feet and allowing it to fall into the kettle; in this way the metal is also exposed to atmospheric influences, and a scum separates as before. The refined metal is sold as *grain*, *refined*, or *common tin*, according to its quality, though all tin met with in commerce has been more or less refined. For *refined tin* purer ores are employed, the refining is continued longer, and after poling the metal is allowed to stand some time, and only the upper or purer portions are used. The second or ordinary quality, when cast in suitable moulds, is known as *block tin.* A simple test of the commercial quality of tin is to melt the metal at a moderate temperature, and to pour it into an ingot mould. The ingot, if of good quality, should be smooth, bright, and rounded, and should retain this appearance on solidification; if impure it will have more or less sharp edges, and will 'frost' over on solidifying, while very impure metal will be tinged with yellow or purple, according to the amount and nature of the impurities. *Grain tin* is produced by heating blocks of refined tin to a temperature a little below the melting-point of the metal, at which point it becomes very brittle, and is broken either by dropping from a height or by a blow of a hammer.

Uses of tin. The manufacture of tin plates absorbs more tin than any other industry, and of this a separate account will be given. Tin is also largely used for alloying with copper to produce bronze, bell metal, and speculum metal, while in combination with other metals tin produces a number of useful alloys, to be afterwards described, among which may be mentioned pewter, Britannia metal, plumber's (or soft) solder, Queen's metal, type metal, fusible metal, &c. Though tin is comparatively brittle at ordinary temperatures, it becomes very malleable at about 100°C., and can then be rolled into thin sheet or foil, for which there is a considerable application, and which was formerly much used, in the form of an amalgam, for the 'silvering' of mirrors. On account of its power of resisting atmospheric influences and the action of vegetable acids, tin is also used for the manufacture of pipes for brewers, distillers, and other purposes. For similar reasons lead pipes are sometimes tin-lined. Pots, pans, kettles, and other culinary utensils are frequently *tinned* inside. The process is very ancient, and extremely simple. The surface of the vessel to be tinned (which may be of copper, brass, or iron) is carefully cleaned and brightened, and a little ammonium chloride (patented for this purpose by John Bootie in 1768) is often rubbed over the surface. Some tin and a little powdered resin is now melted in the vessel, and is wiped over the surface with tow. By this means a skilful workman rapidly produces a uniform coating of tin, which resists considerable wear, and yet weighs, according to the experiments of Bayen, less than a milligramme per square inch of surface. No wonder that Pliny states, with surprise, that copper when tinned does not increase in weight! Tin salts are also used for tinning brass and copper wire, and as mordants in dyeing.

The average production of tin in Britain in recent years is about 10,000 tons per annum; the price is subject to considerable fluctuations, but may be taken as about 100*l.* per ton. In December 1887 this rose to 167*l.* for colonial tin, while the average price in 1878 was only 62*l.* per ton. In 1889 only three British mines produced over 50,000*l.* worth of tin ore, viz.:—

Dolcoath	£114,029
Carn Brea	61,950
East Pool	56,060

The imports in the same year were as follows:—

From Straits Settlements	£2,023,254
,, New South Wales	606,104
,, Other countries	167,916
Total value	£2,797,274

The exports for the same year were valued at 1,629,139*l.*; this, with English production, would leave about 2,000,000*l.* for home consumption, of which probably about one-half was used in the tin-plate trade.

Alloys of tin. The alloys of tin are of great practical importance, and have naturally attracted considerable attention, though it is to be regretted that accurate information is still much wanted in respect of many of their physical and other properties. For convenience of study the alloys of tin may be divided into two classes, the first in which the properties of the resulting alloy is entirely different from the mean of the constituents, while the second class includes those alloys some of the most important properties of which agree very closely with what might be anticipated from the properties of the constituent metals. The first class is typically represented by the alloys of copper and tin, which include the important alloys known as *bronzes*, *gun metal*, *bell metal*, &c. Tin itself is weak, soft, readily fusible, and of a nearly white colour, while copper is strong, tough, moderately hard, and of a characteristic red colour. On adding tin to copper, however, in gradually increasing proportions a succession of alloys is obtained with properties which are utterly different alike from those of each other and from their constituent metals. Thus an addition of about 5 per cent. of soft weak tin to copper produces a tough strong alloy, which still retains a fairly characteristic copper colour, but which is much harder than copper, and is suitable for medals or coinage, but the hardening effect of tin is so great that already the practical limit has been reached for coinage purposes. On adding 5 per cent. more tin we have an alloy which is still harder, so much so that it has to be cast instead of being rolled or drawn, and the alloy possesses a rich yellow colour. With a little more tin an alloy suitable for the hardest bearings is produced, and with still more tin we have the alloy used for small bells, and which is sonorous, but shows considerable brittleness when cold, but which may be worked at a low red heat. With still more tin an alloy suitable for the largest bells is obtained; brittleness is more marked, and the fracture is dull earthy grey, and it is only when the metal has been worked or burnished that a yellow colour is visible. But on continuing the addition of tin, which is one of the softest of the common metals, the alloys become more and more brittle, until with about 33 per cent. the alloy can easily be pounded in a mortar, and possesses a white colour, with a more or less pronounced blue shade. This alloy is thus utterly different alike from its constituents and from either of the other alloys previously mentioned. As examples of the second class of alloys of tin, in which the properties of the alloy are approximately what would be expected from the characters of the constituents, the combination with zinc or with lead may be taken. Tin and zinc unite in all proportions, and the colour, hardness, ductility, &c., of the alloys are what would be anticipated from a mixture of the two constituents. Tin and lead also unite in all proportions to form a series of alloys, all of which are nearly white in colour, and are soft, malleable, and readily fusible, like the metals themselves. Tin-lead alloys, however, furnish a characteristic illustration of the fact that the melting-point of mixtures or alloys is almost invariably lower than what might be anticipated from the known melting-points of the pure substances. This rule is very generally observed, both in salt solutions, with mixtures of salts, and with mixtures of organic substances (Guthrie, P. M. [4] 49, pp. 1, 206, 266; [5] 1, pp. 49, 354, 446; 17, p. 462; 6, p. 35). Common, or soft, solder is an alloy of tin and lead, the best proportions being very nearly 2 parts of tin to 1 of lead. The melting-point of this alloy, calculated from the melting-points of its constituents (Pb = 327°, Sn = 228°), would be 261°C., but the lowest melting-point in this series of alloys actually observed is 180° (Turner, B'ham. Phil. Soc. [4] p. 318) and the composition of the alloy was very nearly 2 parts of tin to 1 of lead. A number of investigators have examined these alloys of tin and lead, including Küpffer, Pillichody, and more recently Laurie (C. J. 1889, 678), and the results of the determination of the composition of the lowest melting-point alloy vary from about 60 to 65 per cent. of tin. There appears to be no indication of a definite alloy of tin and lead in atomic proportions, and the fact that on cooling one alloy crystallises out after another has doubtless led to the differences observed in the results of various experimenters. In addition to their use for solders the tin-lead alloys have an important application in the form of *pewter*, the toughest and hardest variety of which contains about 3 parts of tin to 1 of lead. Alloys of tin and antimony belong to the same class as those previously mentioned, and a mixture of 4 parts of tin with 1 of antimony is used for one kind of type metal. Tin also enters into the composition of Britannia metal, the proportions being as follows (Greenwood, Metallurgy, i. 211):—

	Britannia metal			Queen's metal
	For spinning	For rolling	For casting	
Tin . .	94	90	84	75
Antimony .	5	7	10	8·5
Copper .	1	3	4	—
Bismuth .	—	—	2	8
Lead . .	—	—	–	8·5

Britannia metal has a somewhat considerable application on account of its white colour, and the fact that it takes a good polish and resists the influence of the atmosphere; its low conductivity for heat also renders it very suitable for some purposes. This manufacture was introduced by Jessop and Hancock about 1770.

Type metal varies considerably in composition, consisting essentially of antimony and lead; but for small type tin is commonly added, and in some cases considerable proportions of tin are employed. A similar alloy is also employed in the bearings of heavy machinery, and is known as *white metal.* Tin is also a constituent of the various *fusible alloys*, one of the best known being *Wood's* alloy, which consists of 4 parts of tin with 4 of lead, 8 of bismuth, and a little cadmium, and which fuses at 63°C. Fusible alloys are used chiefly for taking rapid impressions of objects which would frequently be injured by the use of metal melting at a higher temperature, and also for safety plugs in steam boilers &c.

Tin-copper alloys. *History.*—Copper is one of the few metals which have been known from prehistoric periods, and, like silver and gold, is in the pure condition too soft and ductile for many useful applications. The ancients, therefore, prepared various hard copper alloys or bronzes, which were used for many purposes to which iron and steel are now applied. The elements added to give hardness were arsenic, iron, or preferably, when obtainable, tin. A very ancient Egyptian knife-blade (1400 B.C.) examined by Dr. Percy (Metallurgy, i. 504) consisted of copper with 2·29 per cent. of arsenic and 0·43 per cent. of iron; such a material would, of course, form an indifferent cutting tool.

The Hindoos have for many centuries produced a variety of bronze for coins and statues, which was hardened by the presence of iron. Dr. Percy mentions an ancient Indian coin which contained 5·06 per cent. of iron, the remainder being copper (*l.c.*), while in the Birmingham Art Gallery there is one of the earliest known images of Buddha, which is believed to be 2,500 years old, and which was found by Daniel Forbes to contain 91·50 per cent. of copper and 7·59 per cent. of iron. With the introduction of tin by the Phœnicians came the use of bronze in Egypt, Assyria, Greece, and all the important countries of the ancient world. Of these bronzes, numerous examples are preserved, and the composition recommended for various purposes was very similar to that which is used at the present day. Thus Pliny states (Thomson, Hist. Chem. i. 57) that the Romans made their pans for boiling from a mixture of 100 lbs. of copper and 3 to 4 lbs. of tin, while for statues to every 100 lbs. of copper, consisting of one-fourth old copper and three-fourths new metal, 12½ lbs. of tin was added. Brass was not known, or at all events was not in general use, until shortly before the Christian era, and the references to brass which so frequently occur in the Old Testament have to do either with copper or bronze, and not with alloys of copper and zinc.

Constitution of copper-tin alloys. Previous to the researches of Matthiessen, or till about thirty years ago, it was customary to regard alloys as examples of chemical combination, and most experimenters prepared and studied alloys of definite atomic proportions. An example of this method of working is to be found in the researches of Mallet on the tin-copper alloys (Brit. Assoc. Rep. ix., 'Construction of Artillery,' p. 82). The remarkable change in properties which results when tin and copper are alloyed was used as an argument in favour of the view that definite chemical compounds were produced. The result of more recent investigations, however, tends to show that though in some cases definite atomic combinations actually do occur, still these are comparatively few; while the other alloys, which constitute the vast majority of those in use, are either solidified solutions of a definite alloy in an excess of one or other of the constituent metals, or are simply mixtures of the two or more metals present in the alloy. In the tin-copper series there is good evidence of the existence of a definite alloy Cu_3Sn containing 61·64 per cent. of copper, while there is considerable reason to believe that Cu_4Sn, containing 68·18 per cent. of copper, also exists. Thus Calvert and Johnson (P. T. 1858), in investigating the conductivity for heat of these alloys, found a maximum conductivity corresponding to Cu_3Sn, and a minimum conductivity corresponding to Cu_4Sn. Some very interesting determinations by Riche (C. R. 55, 1862, and more completely A. Ch. [4] 30, 361) show two maxima, corresponding to Cu_3Sn and Cu_4Sn. These experiments have also received strong support from the induction balance curve of Roberts-Austen (P. M. 1879, ii. 57), which shows two distinct breaks corresponding to Cu_3Sn and Cu_4Sn. The determinations of relative electric conductivity by Lodge (P. M. 1879, ii. 554) also show a very distinct maximum at Cu_3Sn and a minimum conductivity corresponding to Cu_4Sn. Laurie has recently examined these alloys from the standpoint of the electro-motive force produced in a standard cell, and concludes that there is very definite evidence of the existence of Cu_3Sn, but Laurie failed in this way to obtain any proof of the existence of Cu_4Sn (C. J. 1888, 109; 1889, 678).

The evidence in favour of Cu_3Sn is therefore exceedingly strong, while that in favour of Cu_4Sn, though not quite so complete, is still good, and at present there is no trustworthy evidence in support of any other atomic combinations. These facts, when considered in connection with the known characters of the two alloys in question, give a key to the peculiar characters of the useful tin-copper alloys. The two definite alloys are white, hard, and brittle, and practically all the alloys used in the arts, except speculum metal, contain more copper than $Cu_4Sn = 68{\cdot}18$ per cent. Cu. Hence bell metal, gun metal, and other varieties of bronze must be regarded as mixtures of one or more definite alloys with an excess of copper, and these tend to separate more or less completely during solidification. This separation is particularly marked with large castings rich in copper, as in *gun metal*, which was in former times largely used for ordnance.

The production of such castings requires special precautions, which cannot be described here. For details, see Mallet 'On the Construction of Artillery,' 1856; also Reports of the United States Chief of Ordnance, 1880, 126, 189; 1884, 369. These latter reports contain some of the most important observations which have yet been published with regard to this variety of bronze. It is stated that the best proportion for such purposes is 91 of copper to 9 of tin. This is best cast in a mould or 'chill' of cast iron, and 100 tests of metal so prepared gave an average tensile strength of 21·9 tons per square inch, the maximum being 24·8 tons and the minimum 16·5 tons. It should be mentioned that these values are higher than those usually obtained in this country, where the metal is generally cast in sand moulds.

Composition of principal tin-copper alloys. The following list is based on that given by Holtzapffel (Mechanical Manipulation, i. 270).

Tin, 0 to 5 per cent. A small quantity of tin is sometimes added to copper for engraver's purposes to give crispness. About 5 per cent. was used by the Romans for pans, and for ancient flexible bronze nails. A similar alloy is now used for bronze coinage and medals, often with a little of the tin replaced by zinc; also for engineers' soft gun metal or 'brasses.'

7 per cent. Slightly harder alloy; suitable for mathematical instruments &c.

8·5 per cent. Rather harder; fit for wheels to be cut with teeth.

8 to 12 per cent. Soft bronze statues of the ancients. These alloys are harder than the preceding, and mark the extreme limit for coinage purposes. Also used for brass ordnance, 9 or 10 per cent. of tin being preferred. Medium engineers' 'brasses' contain 10 to 12 per cent. of tin.

12 to 14·5 per cent. Hard bronze of the ancients, used for weapons and tools. These proportions are also used for engineers' hard bearings.

16 per cent. Soft musical bells.

18 to 20 per cent. Chinese gongs and cymbals.

20 per cent. Small house bells; Indian gongs.

22 per cent. Large house bells.

24 per cent. Limit for large church bells.

About 33 per cent. Speculum metal (*v.* Tr. 1840, 503).

About 66 per cent. 'Temper,' an alloy used for addition to tin and lead to harden pewter.

It has already been mentioned that the addition of a small quantity of tin to copper prevents it rolling well when hot, and the addition of a little more tin destroys its malleability when cold. Bronze is tempered by an exactly opposite process to that used in the case of steel, namely, the alloy is heated to redness and then rapidly cooled in water.

For the majority of purposes bronze is melted in crucibles of fireclay or plumbago, the charge being about 90 lbs. For large castings a reverberatory furnace is often employed, though such work is sometimes performed by means of a large number of crucibles. It is recommended that the copper should be well melted and kept in fusion for some time before the tin is added, if strong castings are required. Founders also prefer to use some new metal in every charge, and not merely to re-melt scrap. The oxidation which takes place during melting removes some three or four parts of copper to one of tin; the result is, therefore, that the alloy, which contains about nine parts of copper to one of tin, tends to get poorer in tin by remelting, and due allowance must be made for this loss, even though it may appear to be slight, as small differences in composition often exert a most important influence in tin-copper alloys.

Bronze bearing metal. According to Dudley (Jour. Franklin Inst. 133, 81, 161; S. C. I. 11, 460), the following composition is very suitable for bearings for locomotives and similar purposes: copper, 77; tin, 8; lead, 15. The presence of lead in bearings very much diminishes the loss of metal caused by wear, and also reduces the local heating of the journals. Phosphor bronze and other varieties of bearing metal for similar purposes to the above often contain about 10 p.c. of lead, and the wearing properties of the alloys is chiefly connected with the proportion of copper and tin to lead. The presence of tin is necessary in order to obtain a uniform alloy, as lead and copper alone do not unite well. With too much tin the alloy wears more rapidly and becomes more heated. The presence of phosphorus and arsenic gives solidity to the castings, but with suitable proportions of tin and lead, as above, alloys are obtained which wear even better than standard phosphor bronze with the following composition: copper, 79·7; tin, 10; lead, 9·5; phosphorus, 0·8 p.c.

Phosphor bronze is an alloy containing copper, zinc, and tin in various proportions, and which also contains a small quantity of phosphorus, introduced in the form of phosphor tin. This alloy has met with considerable favour where special strength or power of resisting wear (as with bearings for quick running machinery) is required. Similar alloys containing manganese, which is added in the form of ferro-manganese, have also met with a limited application, and are known as *manganese bronzes. Silicon bronze*, made by the addition of copper silicide, is used for conductivity wire, though some of these so-called bronzes contain very little or no tin.

Tin plates. *History.*—Although the art of tinning brass and copper was well known to the Romans (*v. supra*), the production of sheet iron coated with tin, or 'tin plate,' is of a considerably later period, though the exact date of its introduction is unknown. The art was, however, probably of German origin, and existed in Bohemia for many years prior to 1620. About this time the manufacture was introduced into

Saxony through the efforts of the then reigning Duke, and speedily developed into a thriving industry. Shortly afterwards, two unsuccessful attempts, with which M. Réaumur was connected, were made to introduce the manufacture into France. About 1670 an English company was formed to start a tin-plate works in this country, and Mr. Yarranton was sent to Germany to learn the art. Works were started at Pontypool, and met with some success, but were stopped, owing to the grant of a patent for the manufacture to E. Hemming in 1691. Works were, however, once more started in 1720 at Pontypool, and these were gradually followed by others, particularly in South Wales, which has gradually become the most important seat of the manufacture in the world. In the earlier processes of manufacture the plates were hammered by hand from iron made in the charcoal hearth, while the surface was cleaned from scale by immersion for several days in sour barley-water, instead of for a few minutes in dilute sulphuric acid, as at present.

In 1728, the *rolling* of sheets was introduced by Major Hanbury, of Pontypool, while sulphuric acid was substituted for barley-water in 1806. The rolling of tin plates as they leave the tin pot, which saves metal and improves the surface, was introduced by Morewood (who took out many patents for coating metals) in 1866, since which time a great variety of machines have been introduced for use in the tinning process, though most of them have met with a very limited use.

During the last twenty years great changes have been introduced. In the first place, pickling machines have superseded hand labour, while iron made in the old-fashioned open-hearth refinery (or puddling furnace for second qualities) has been generally replaced by steel. Siemens' steel was used about 1875, Bessemer steel about 1880, and basic steel was introduced a few years later (*v.* P. W. Flower, 'Origin and Progress of the Manufacture of Tin Plates,' J. Iron and Steel Inst., 1886).

The number of tin-plate works in this country in 1885 was ninety-six, of which eighty-one were in South Wales and Monmouthshire and fifteen elsewhere. The production for 1884 was distributed as follows:—

Exported to the United States	3,472,782 boxes.
Home consumption . .	1,832,326 ,,
Exported to other countries .	1,648,219 ,,
Stock	241,880 ,,
Total . .	7,195,207 boxes.

The maximum annual production hitherto recorded was reached in 1889, when no less than five and a half million boxes were exported to the United States.

Production of tin plate. The metal used for rolling into sheets is, as above stated, either wrought iron of special quality, which in former times was made in refineries using only charcoal, or more generally at present very mild steel is employed, Siemens' steel being in most demand for this purpose. The bars are cut into suitable lengths, and each length is heated to redness, and then passed through 'chilled' rolls until its length is about doubled; the plate is then folded across the middle, re-heated, and again rolled. The re-heating, folding over, and rolling is repeated until a sheet of the proper thickness is obtained, sometimes as many as thirty-two thicknesses being rolled together as one piece in this way. The sheets are then cut to size with shears and separated, when they should part readily if the operation thus far has been successfully conducted. The 'rough black plates' so produced should be free from streaks or 'spilly' places, and should be uniformly coated over with a black scale of oxide. This is now removed by 'pickling' in warm dilute sulphuric acid for about twenty minutes, and by subsequent washing and rubbing with sand and water. The sheets are next annealed in wrought-iron boxes, which are usually about 2 feet square, but vary in size; the upper part is in the form of a bell for ready removal, and to prevent the entry of air the joint is stopped by being covered with sand. The annealing requires about ten hours, and is conducted in a large furnace maintained at a cherry-red heat. The pots are then withdrawn and allowed to cool, after which the sheets are cold-rolled, to improve the surface and give the smoothness and uniformity which is necessary to produce a good tin plate. The cold-rolling renders the plates somewhat hard, and they are therefore annealed once more, usually in cast-iron pots, as it is not necessary in the second annealing to use so high a temperature or as long a time as in the first case. The sheets are now finally pickled in weaker sulphuric acid than was used in the previous pickling, and after being again rubbed with sand are immersed in water preparatory to tinning.

The tinning apparatus, or 'stow,' varies somewhat with the size and quality of the plates; with very large plates the bath of tin is contained in a basin-shaped pot, while for large sizes and inferior qualities the plates are frequently manipulated entirely by machinery during the tinning process.

The ordinary form of apparatus consists of five baths or pots, called respectively (1) the grease pot, (2) the tin-man's pot, (3) the washing pot, (4) the dipping pot, (5) the grease pot. Formerly two other pots were used, but these have been rendered unnecessary by the introduction of rolls. The grease pot contains melted grease, such as tallow or palm oil, and in this the sheets are dipped until all moisture has been removed and they are uniformly coated with grease. They are next dipped into the tin pot, which contains melted tin covered with a layer of grease, the latter being sometimes replaced by a bath of zinc chloride or 'killed spirits.' The sheet now receives its first coating of tin, which, however, is not perfect, and to complete the tinning the sheet is dipped into the first compartment of the washing-pot, where it remains until a uniform coating is produced. The plate is now taken out and rapidly examined by the workman, who wipes over the surface with a brush, and to remove the marks of the brush rapidly dips the plate into the second compartment of the same pot, which contains the best tin, and then transfers it to the grease pot, where it passes through a pair of rolls, which squeeze off the excess of tin and improve the surface. Formerly the plate remained for about ten minutes in the grease pot, during which time the excess of tin drained off. The plate was afterwards transferred to the 'cold pot,' after which the lower part was inserted in the 'list' pot, which contains a little tin at a comparatively high temperature, and which rapidly removes the thick edge of tin which had accumulated at the bottom of the plate. The plates, after coating with tin, are then cleaned from grease, usually by rubbing with bran and finishing with the woolly skin of a sheep; they are afterwards separately examined for defects, and, after classification, are packed in the familiar flat wooden boxes and branded for market (*v.* E. Trubshaw, J. Iron and Steel Inst. 1883, i. 252).

Tin plates in France. At Hennebont in the department of Morbihan is an important tinplate works, employing about 700 hands, and producing over 12,000 tons of tin plates and sheet iron per annum. The works were established in 1860, and manufacture their own steel in the basic Siemens' furnaces, the use of refined or puddled iron having been completely abandoned. The steel is cast into ingots, which are re-heated, and then shaped and cut by a steam hammer and rolled into bars. The bars are about 4 inches wide, 0·4 inches thick, and are cut into pieces about 8 inches long, which are heated and rolled into eighths as previously described. The subsequent processes of pickling, annealing, cold rolling, annealing, pickling, and tinning are conducted as in this country, except that chopped rice straw is used for cleaning the sheets (*Iron*, vol. 34, p. 52).

For a description of the process of manufacture of tin plates in Germany, which does not materially differ from that above described, *v.* D. P. J. 250, 231.

Manufacture of tin plates in the United States. For some years past, at least one half of the tin plates manufactured in the United Kingdom have been exported to the United States of America. But by the M'Kinley Tariff Act, which came into effect on July 1, 1891, the duty on tin plates imported into the United States has been more than doubled, with the intention of creating a tin plate industry in America. The quantity of tin plates actually manufactured in America up to the present has been small, the estimated production of works in operation and in construction being about 60,000 tons per annum; but there is every probability of a largely-increased production in the immediate future. Hitherto, American manufacturers have been generally content to copy the methods adopted in South Wales. T. T.

Dry assay of tin ores. Hofman finds that Winkler's method of assaying black tin stone gives results averaging 65·96 per cent., or 1·88 per cent. too low, the figures disagreeing amongst themselves up to over 3 per cent. The process consists of reducing together 5 grms. each of cassiterite and cupric oxide with 15 grms. of black flux, 1·25 grms. of borax, and a little salt as a cover. A similar experiment is conducted without the cassiterite, and the copper obtained in the one case deducted from the alloy in the other gives the amount of tin. The following modifications of this method were tried: increasing the amount of charcoal, using chalk-lined crucibles, omitting the salt and increasing the potassium carbonate, and Rickett's modification of adding argol; but they all gave worse, and in some instances very variable, results.

The iron method—reduction with hæmatite, charcoal, and potassium cyanide or fluorspar—gave unsatisfactory results. The same may be said when a mixture of ferro-cyanide and cyanide was used, and also when any of the Cornish methods were employed. So far, with fairly pure cassiterite only two methods have proved satisfactory, viz. the German and the pure cyanide methods. Hofman has attempted to prove which of these two methods gives the best results when the cassiterite is mixed with those minerals likely to be naturally associated with it. The minerals used were quartz, felspar, mica, tourmaline, garnet, and columbite. Mixtures of the purified cassiterite ore with varying proportions of each of these minerals were assayed by both methods, the percentage of tin being calculated on the cassiterite ore present. The charges were so regulated that the flux in the German assay was always equal to three times the quantity of ore plus the mineral, and in the cyanide assay to six times the quantity. In the latter case four parts of cyanide were mixed with the ore; one part was used to coat the crucible bottom, and one part as a cover. In all cases the cyanide method gave more concordant, and less prejudicially affected, results than the other. The results of the German assays fluctuated greatly as the amount of mineral present increased. Thus, in the case of quartz and albite the results were lower as the quantity of mineral was increased, the respective figures being, with 37·5 per cent. of each mineral, 60·7 and 60·2 per cent.; the corresponding cyanide figures being 63·90 and 65·30 per cent. (the real percentage of tin was 67·84). The tin buttons, moreover, in the German assay with albite contained iron, while those by the cyanide process were free, the temperature of fusion being too low to cause decomposition of the albite.

With muscovite, tourmaline, garnet, and columbite the results with the German method were very unreliable, being sometimes too high and very ferruginous, and sometimes too low, varying from 82 per cent. with 50 per cent. of garnet to 46 per cent. with 44 per cent. of tourmaline. The cyanide method gave fairly good results in all the above cases, very little iron getting into the buttons, except in the case of garnet, when the result was 69·89 per cent., with 37·5 per cent. of mineral present. With the same quantity of muscovite, tourmaline, and columbite the assays were respectively 63·3, 64·7, and 66·0 per cent. Consequently, where anything like a true result is required the cyanide assay is by far the most to be relied upon, and should be employed in cases of buying and selling, although in concentration works, where comparative results and large numbers of assays are required, the question of cost must be considered, and the cheaper German method might satisfactorily be adopted.

Hofman emphasises the importance of properly preparing the ore for assay, and states that the ordinary method of grinding the whole sample to a uniform size is not suited to the tin ores of the Black Hills, chiefly on account of the preponderance of mica. Hence a preliminary sizing is advantageous. The ore while being pulverised is screened through a series of sieves Nos. 20, 40, 60, and 80, the different-sized screenings being then washed. This method gives purer concentrates, and necessitates less loss of cassiterite, as the material has been washed without excessive grinding, which in the present process reduces the brittle cassiterite to a slime, while some of harder associated minerals are only converted into sand. The subsequent treatment of the concentrates mentioned in the first part of the paper is recommended, as the roasting renders the cassiterite more friable and more readily reducible, the assays in some cases showing a difference of 0·5 per cent. between the raw and roasted ores in favour of the latter (Part ii., H. O. Hofman, Technol. Quarterly, 3, 261–280; S. C. I. 9, 1,154; *v.* Rennie and Derrick, S. C. I. 1892, 662).

Tin salts and oxides. A monoxide, *stannous oxide* SnO, and a dioxide, *stannic oxide* SnO_2, each of which gives rise to a distinct series of salts, are known, the former acting as a base and the latter acting as either base or acid. Oxides of the composition Sn_2O_4, $SnO.3SnO_2$, and $2SnO_3H_2O$ are also said to exist.

Stannous oxide SnO is obtained as an olive-brown anhydrous powder, when stannous oxalate is heated out of contact with the air, or as a white precipitate of the composition $2SnO.H_2O$, with evolution of carbon dioxide, when stannous chloride and an alkaline carbonate are mixed in solution. It may also be obtained as a bluish-black anhydrous powder by heating a mixture of 4 parts of stannous chloride with 7 of sodium carbonate, and lixiviating the resultant mixture of stannous oxide and sodium chloride (Sandall, J. pr. 14, 254). The anhydrous oxide may also be obtained from the hydrous form as follows: (1) as a black powder by heating it out of contact with the air; (2) in minute cubes by digestion with acetic acid at 56°; (3) of a brilliant scarlet colour, which becomes brown on rubbing, by evaporating a dilute solution of ammonium chloride containing stannous chloride in solution until the chloride commences to crystallise (Fremy, B. J. 24, 133; 25, 172; A. Ch. [3] 12, 460); (4) as small black shining crystals, which, when heated to 258°, decrepitate and swell up, with production of soft olive-green laminæ, by prolonged digestion with a weak solution of potash at the ordinary temperature (Fremy, *l.c.*). A stronger solution dissolves the oxide and ultimately deposits it in crystals, the deposit from a solution of 4 parts of potash in 10 of water containing potassium stannate and tin, the former produced by absorption of atmospheric oxygen. Fremy also describes various red, black, brown, and other forms of this oxide.

Stannous oxide becomes incandescent, and forms stannic oxide, when heated in the air. Carbon or hydrogen reduces it to metal at a red heat. It dissolves in acids, with production of stannous salts, and in potash or soda, but not in ammonia. The soda solution is employed in calico printing and dyeing under the name *sodium stannite*, and is prepared as described under *sodium stannate* (p. 841).

A so-called *sesquioxide* Sn_2O_3 is obtained as a slimy grey precipitate by the action of recently-precipitated ferric hydroxide on a solution of stannous chloride (*v.* Fuchs, Kastner's Archiv für Chemie und Meteorologie, 23, 368; J. pr. 5, 318; and Berzelius, P. 28, 443; B. J. 13, 110).

This body is readily soluble in ammonia and in concentrated hydrochloric acid. It does not appear to form definite salts. Its hydrochloric acid solution acts like a mixture of stannous and stannic chlorides. An orange-yellow oxide of the composition $SnO.3SnO_2$ is obtained by digesting metastannic acid in cold aqueous stannous chloride (Fremy, J. Ph. [2] 1, 344).

Stannic oxide SnO_2 occurs as *cassiterite* or *tinstone*, varieties of which are known as *stream tin*, *wood tin*, *toad's eye*, &c. Daubrée (Ann. M. 20, 65) has pointed out that, with the exception of quartz, the minerals most frequently associated with tin ore are fluorine compounds.

Stannic oxide is obtained as an anhydrous white powder of sp.gr. 6·7122 at 4° (Joule a. Playfair, C. J. 1, 128) when tin is heated until it burns in the air. The powder is converted into microscopic quadratic crystals resembling the native oxide when heated in a current of hydrochloric acid gas (Deville, C. R. 53, 161). The oxide may also be obtained in trimetric crystals, and is therefore dimorphous (*v.* Daubrée, Ph. C. 1849, 821; Levy a. Bourgeois, C. R. 94, 1365).

Stannic oxide is reduced to metal when heated with hydrogen, carbon, potassium, or sodium. It dissolves in fused potassium bisulphate, but separates from the mass when treated with water. When fused with sulphur, stannic sulphide is formed, with evolution of sulphur dioxide.

The anhydrous oxide is insoluble in acids, except in concentrated sulphuric, with which it forms a syrup decomposed by dilution, with precipitation of the oxide. It dissolves in aqueous or fused alkalis, with formation of stannates.

Stannic oxide, prepared by igniting metastannic acid, is known as 'putty powder,' and used for polishing plate and for imparting whiteness to enamel or glass.

The oxide exists in several stages of hydration, the most important of which constitute stannic and metastannic acids (*v.* Fremy, A. Ch. [3] 12, 466; 23, 393; Weber, P. 122, 358). Between these acids, which are described below, a number of bodies of intermediate composition, corresponding with the varieties of silicic acid, are said to exist (Musculus, C. R. 65, 961).

Perstannic oxide SnO_3. W. Spring (Bl. [3] 1, 180) has obtained a body of the composition $H_2Sn_2O_7$, probably a hydrate of this oxide, by dialysing the turbid solution obtained by adding hydrated barium peroxide in excess to a solution of stannous chloride in hydrochloric acid, and evaporating the solution of the colloid on the water-bath.

Stannic acid H_2SnO_3 is obtained by precipitating stannic chloride with ammonia, or by addition of calcium or barium carbonate to a solution of stannic chloride in quantity insufficient to precipitate the whole. It then forms a gelatinous substance, slightly soluble in water and of acid reaction. When dried spontaneously it forms translucent lumps resembling gum arabic.

According to Fremy (*l.c.*), it has the composition $3SnO_2.7H_2O$ when dried in a stream of dry air, $SnO_2.H_2O$ when dried *in vacuo*, and $3SnO_2.2H_2O$ when dried at 140°. Weber (*l.c.*) states that its composition when dried spontaneously in dry air is $SnO.H_2O$, and is identical with that of air-dried metastannic acid; while, according to Carnelley and Walker (C. J. 1888, 83), it has the composition $3SnO_2.H_2O$ a little above 360°, and on further slight rise of temperature loses water and turns from its previous dirty-brown colour to a pale-yellow body of the composition $7SnO_2.2H_2O$. It becomes anhydrous at 630° to 655°.

A colloidal stannic acid is known (*v.* Graham, Tr. 151, 213, and Van Bemmelen, Rec. Trav. Chim. 7, 87).

Stannic acid forms a large and important series of salts, most of which are crystalline. The alkaline stannates are soluble, and may be prepared by dissolving the precipitated oxide in the alkaline hydrate. The others are mostly insoluble, and are best obtained by double decomposition. The potassium and sodium salts are the only ones of technical importance. The stannates have been investigated by Fremy (A. Ch. [3] 12, 462; 23, 393), Moberg (J. pr. 28, 230), Marignac (Ann. M. [3] 15, 277), Ordway (Am. S. [2] 40, 173), and Ditte (C. R. 94, 1114; 96, 701).

Sodium stannate Na_2SnO_3 usually occurs in six-sided tables of the composition $Na_2SnO_33H_2O$ (Moberg, Marignac, Ordway, *l.c.*), which are less soluble in hot than in cold water. According to Ordway, 100 parts of water dissolve 67·4 parts at 0°, and 61·3 parts at 20°.

Crystals of the above composition are deposited from a hot alkaline solution, but the salt may also be obtained with 8, 9, or 10 molecules of water. The form crystallising with 9 molecules is said to be obtained in oblique rhombic prisms by recrystallising the commercial salt (Jonas, C. C. 1865, 607); while, according to Haeffely (D. P. J. 144, 66), crystals of the composition $Na_2SnO_3.3H_2O$ are deposited from hot concentrated solutions of 1·3 sp.gr., but re-dissolve on cooling to a solution of 1·35 sp.gr., from which crystals containing 8 molecules of water are gradually deposited.

Copper is readily tinned by immersion in a solution of the salt.

Sodium stannate is largely used, under the name of 'preparing salt,' as a mordant in dyeing and calico-printing, the fabric being first passed through a solution of the stannate, and then through weak sulphuric acid, which precipitates the hydrated oxide on the fibres.

For preparing this salt on the large scale, the original processes patented by J. Greenwood, J. Mercer, and J. Barnes (Pat. No. 10,757, 1845), J. Young (Pat. No. 12,359, 1848; 12,744, 1849), and Haeffely (Pat. No. 603, 1854), are still used with some modifications. A number of other processes are mentioned in the list of patents relating to tin salts (*infra*).

The process of Greenwood, Mercer, and Barnes consists in heating 22 lbs. of caustic soda in an iron crucible until evolution of water ceases, and then adding 8 lbs. of sodium nitrate and 4 lbs. of sodium chloride, followed, when the mass is nearly fused, by 10 lbs. of feathered tin, with constant stirring until deflagration ensues. The mixture then becomes white hot and pasty, and is wholly converted into the stannate.

For preparing sodium '*stannite*' a mixture of 4 lbs. of sodium chloride, 1 gallon (13·5 lbs.) of caustic soda, 1 lb. of sodium nitrate, and 4 lbs. of tin is heated in an iron crucible, and the dry powder finally obtained is stirred so long as ammonia is evolved.

Young's processes—most of which are described below—consist mainly in the preparation of the stannate directly from the ore, thus avoiding the cost of obtaining and re-oxidising the metal.

By one process the native or prepared oxide is boiled in an iron pot with a quantity, varying with the tin value of the ore, of 22 per cent. soda lye, the heat being gradually raised to about 600°F., at which combination takes place. When the operation is completed, which is ascertained by removing a portion and seeing how much dissolves, the mass is cooled in another vessel and is dissolved, filtered, or decanted, and recrystallised or sold in solution.

In another process, the ore is heated to redness with one and a half parts of sodium nitrate in a current of steam with constant stirring. The stannate is produced, with evolution of nitrous fumes and nitric acid. The nitrate may be replaced by one part of salt, hydrochloric acid being then obtained as the by-product.

'Stannite' of soda is obtained by heating the metal with its own weight of caustic soda, with constant stirring. The solution of the stannite may be used in dyeing and printing operations as it is, or it may be converted into stannate, with precipitation of tin as a black powder, by boiling.

The stannate may be obtained direct from the metal by heating a mixture of 20 parts of tin, 16 of soda, and 3 of manganese peroxide to redness, with constant agitation and free exposure to the air. The peroxide appears to act as a carrier of oxygen, and is obtained unchanged at the end of the operation.

In another process, stannate of lime is obtained by roasting in a reverberatory furnace a mixture of the ore with slaked lime. The product is treated with sufficient hydrochloric acid to precipitate the tin as oxide, but not to redissolve any of it, and the precipitate is dissolved in boiling soda lye. The salt may also be obtained by boiling barium stannate, obtained similarly to the lime salt, with sodium sulphate, until all the barium is converted into sulphate.

Haeffely's process consists in the preparation of a solution of 'plumbate of soda' by dissolving 54 lbs. of red lead or 70–80 lbs. of litharge in a solution of 45 lbs. of caustic soda of 70°Tw. The solution is diluted, and 16 lbs. of tin is suspended in it while boiling, so that in four or five hours the lead is obtained as a deposit, which may be readily oxidised for re-use, while sodium stannate remains in solution.

The following process is said to be now employed in an English works (Chem. Zeit. 9, 851):—Ten boilers, arranged in horseshoe form, and each having a central tube whose lower end forms a perforated funnel, are almost filled with granulated tin, and six of them are charged with soda lye of 15°Bé. The liquor is drawn off from each, after a suitable amount of boiling, through a syphon passed into the central tube, and is passed from boiler to boiler until of 30°Bé., when it is allowed to settle in a tank. For preparing 'sodium stannate liquor,' enough common salt is dissolved in the solution to reduce the proportion of tin to 5 p.c.; and for producing the solid the liquid is evaporated and calcined, and mixed with enough sodium chloride to reduce the tin to 42 p.c.

An arsenio-stannate of sodium

$$Na_2O.6SnO_2.2As_2O_5.5H_2O,$$

occurring in shining needles, is sometimes used instead of the ordinary stannate, and is said to give brighter colours and to be more economical. It is prepared by adding nitric acid to a boiling solution of sodium stannate and sodium arsenate, and treating the resulting precipitate of $2SnO_2.As_2O_5.10H_2O$ with excess of soda (*v.* Haeffely, D. P. J. 140, 290; J. Mercer a. W. Blythe, Pat. No. 12,807, 1849). The latter also employ a sodium phospho-stannate for the same purposes.

Potassium stannate K_2SnO_3 is obtained similarly to the sodium salt, and is sometimes employed in dyeing and calico-printing. It crystallises from spontaneously evaporated solutions, in transparent oblique rhombic prisms of the composition $K_2SnO_2.3H_2O$ (Marignac, Ann. M. [5] 15, 277; Moberg, J. pr. 28, 230; and Ordway, Am. S. [2] 40, 173). It becomes anhydrous when heated to redness.

Potassium stannate is insoluble in alcohol, but dissolves in water to an alkaline solution, 100 parts of water dissolving 106·6 parts at 10° and 110·5 parts at 20° (Ordway, *l.c.*).

Cupric stannate $CuSnO_3$ has been employed as a green pigment. It is prepared for this purpose by precipitating sodium stannate with copper sulphate, or by addition of a solution of 118 parts of tin in aqua regia to a solution of 250 parts of copper sulphate, with subsequent addition of soda in excess.

Chromium-tin compounds. A so-called chromium stannate, used for producing a blood-red colour in pottery glaze, is prepared by heating for several hours in a closed crucible a mixture of 10 parts of stannic oxide, 34 parts of calcium carbonate, 5 parts of silica, 1 part of alumina, and 3 to 4 parts of crystallised potassium chromate. The red body produced gives a fine rose-coloured product when washed with dilute hydrochloric acid.

A substance known as *mineral lake*, possibly a basic chromate of tin, possessing a fine lilac colour, is used in colouring paper hangings and for oil painting. It is best prepared by dissolving potassium chromate in 5 or 6 parts of water, and adding to a solution of stannous chloride until precipitation ceases. The damp, washed precipitate is ground with half its volume of nitre, and dried, and the finely-powdered mixture is thrown in small portions into a crucible heated to redness and containing some potassium nitrate. After pouring off the supernatant fused salt, the pale-yellow residue is washed free from alkali, and is calcined at a strong heat in a luted crucible until it becomes dense and acquires the desired colour.

Metastannic acid is obtained as a white insoluble powder, with evolution of nitrous fumes, when tin is treated with strong nitric acid. According to Fremy (A. Ch. [3] 12, 466; 23, 393), its composition when dried in a current of dry air is $SnO_2.2H_2O$, when dried in vacuo or at 100° $SnO_2.H_2O$, when dried at 130° $5SnO_2.4H_2O$, and when dried at 160° $5SnO_2.3H_2O$. According to Weber (P. 122, 361), the acid dried over sulphuric acid has the composition $SnO_2.H_2O$.

Metastannic acid possesses an alkaline reaction, and is insoluble in nitric acid. It swells up in concentrated sulphuric acid, the product being soluble in water and alcohol, but decomposing into the two acids on boiling. Hydrochloric acid converts it into a chloride of metastannic acid, which is soluble in water but not in hydrochloric acid, and which is reprecipitated from solution in the gelatinous form on boiling, or on addition of much hydrochloric acid.

It is insoluble in ammonia, except when freshly-precipitated from a cold solution of a metastannate by an acid, but dissolves in alkaline hydrates and carbonates, with formation of metastannates.

A colloidal metastannic acid is known (*v.* Graham, Tr. 151, 213; Van Bemmelen, Rec. Trav. Chim. 7, 87).

The salts of metastannic acid appear to indicate that the acid has the formula

$$5(SnO_2.H_2O),\ i.e.\ H_2Sn_5O_{11}.4H_2O,$$

but Weber (*l.c.*) considers it to have the same composition as stannic acid.

The metastannates are difficultly crystallisable. When strongly heated, they decompose into stannic oxide and the base. *Potassium metastannate* $K_2Sn_5O_{11}.4H_2O$ is a strongly alkaline salt obtained by dissolving the acid in potash. It is precipitated from aqueous solution by a neutral alkaline salt or by ammonium chloride. *Sodium metastannate* $Na_2Sn_5O_{11}.4H_2O$ is a slightly soluble granular salt obtained like the potassium salt. A hard gummy precipitate of the composition $Na_2Sn_9O_{19}.H_2O$ is obtained by addition of caustic soda to a solution of the above compound of hydrochloric acid and metastannic acid.

Salts of tin with oxyacids. These salts, though numerous, are of little technical importance, but a number of solutions containing them are used in dyeing and calico-printing. *Stannous sulphate* $SnSO_4$ is obtained as a crystalline powder by evaporating *in vacuo* a solution of tin or stannous hydroxide in dilute sulphuric acid. *Stannic sulphate* $Sn(SO_4)_2$ is obtained as a white salt, soluble in dilute sulphuric acid but mostly precipitated on dilution, by dissolving the hydroxide in sulphuric acid. According to Ditte (C. R. 104, 172), a solution of stannic hydroxide in warm dilute sulphuric acid (1 to 8) deposits, on concentration, first radiating needles, then rhomboidal lamellæ, and finally hexagonal prisms, all colourless and all possessing the composition $Sn(SO_4)_2.2H_2O$. He has obtained the same body by the action of sulphuric acid on metastannic acid. The crystals deliquesce to a clear liquid. The solution is decomposed, with precipitation of the hydroxide, on dilution. *Stannous nitrate* $Sn(NO_3)_2$ is obtained by dissolving tin or stannous hydroxide in very dilute nitric acid. According to R. Weber (J. Pr. [2] 26, 121), it is obtained of the composition $Sn(NO_3)_2.20H_2O$, by solution of freshly-precipitated stannous hydroxide in a molecular proportion of ice-cooled nitric acid of sp.gr. 1·20. On cooling to 20°, the nitrate crystallises out in clear plates resembling potassium chlorate. A basic salt of the composition $2SnO.N_2O_5$ is obtained as a white crystalline precipitate by adding a solution of sodium carbonate to the neutral salt in quantity insufficient for complete precipitation. It may also be obtained by digesting the normal salt with stannous hydroxide. It deflagrates at 100°, or on friction. *Stannic nitrate* crystallises in silky tablets from a solution of stannic hydroxide in nitric acid. The so-called 'nitrate of tin' or 'physic' used by dyers is a mixture of stannous and stannic chlorides (*v. Stannous chloride, infra*). A solution of tin in nitric acid is, however, also used in dyeing (*v.* Crookes, Handb. of Dyeing and Calico Printing, 1874, 527). *Stannous acetate*, *oxalate*, *citrate*, and *tartrate* are employed in dyeing and calico printing, being generally prepared by addition of an alkaline salt of the acid to a solution of stannous chloride, or by dissolving the precipitated hydroxide in the acid. Liechtl and Schwitzer (Mittheilungen des Tech. Gew. Museums, 1886, 41) report on the value of some of these as mordants.

Stannous sulphide SnS is obtained as a tough, crystalline, bluish-grey fusible mass by heating tin with sulphur, or in crystalline scales by fusing the sulphide so obtained with stannous chloride and treating the product with dilute hydrochloric acid. It is obtained as a brown powder, which blackens on drying, by precipitating stannous chloride with sulphuretted hydrogen.

Stannous sulphide is insoluble in normal ammonium sulphide, but dissolves in the yellow sulphide and in alkaline polysulphides (*v.* Ditte, C. R. 94, 1419), and, with evolution of sulphuretted hydrogen and formation of stannous chloride, in hot hydrochloric acid. Dry hydrochloric acid gas acts similarly on the warmed, but not on the cold, sulphide (Ditte, C. R. 97, 42).

Stannic sulphide SnS_2 cannot be prepared by simply heating tin and sulphide together, because the heat generated is sufficient to reduce the disulphide to monosulphide, but it may be so obtained when sufficient ammonium chloride or other volatile substance is present to moderate the action. Woulfe (Ptnt. Trans. [1771] 61, 114; also Gmelin's Handbook, 5, 79) describes a number of methods of preparing this body, which was formerly much used for gilding, imitating bronze &c., under the names 'mosaic gold,' 'mock gold,' and 'cats' gold.'

The best preparation is obtained by heating 12 parts of tin, amalgamated with 6 parts of mercury, and ground up with 7 parts of sublimed sulphur and 6 of ammonium chloride, in a glass vessel embedded in a sand-bath. The heat is moderated until white fumes and sulphuretted hydrogen cease to come off, but is then raised to redness. After cooling, the vessel is broken, and the sulphide is found in golden translucent scales or six-sided laminæ of sp.gr. 4·425 (Boullay, 19, 107). The mercury passes off as sulphide. The heat requires careful adjustment, as too low a temperature produces a pale product, while too great heat gives a greyish compound. The mercury may be dispensed with, but an inferior product is then obtained.

When heated, stannic sulphide sublimes, with partial decomposition into sulphur and stannic sulphide. It dissolves readily in alkalis, but not in acids, except aqua regia. It fuses in a current of chlorine, and absorbs 6 molecules of the gas, forming a yellow crystalline compound of the composition $SnCl_4 2SCl_4$ (Rose, P. 42, 517). When heated with iodine in a current of carbon dioxide it gives a brown, crystalline, fusible mass of the composition SnS_2I_4 (Schneider, J. pr. 79, 419).

The dirty-yellow precipitate obtained by passage of sulphuretted hydrogen through a solution of a stannic salt consists of a mixture of stannic sulphide and stannic hydroxide, which dissolves in alkaline sulphides, with formation of thiostannates (Kühn, A. 84, 110), and also in alkalis and hydrochloric acid. Ditte (C. R. 95, 641) describes several double sulphides or thiostannates and also seleniothiostannates.

Thiostannic acid SnH_2S_3 may be obtained as a yellow precipitate, which becomes almost black on drying, by addition of dilute hydrochloric acid to a thiostannate.

Stannous selenide SnSe is obtained with incandescence when selenium is heated with tin, as a light-grey lustrous body of crystalline fracture, not reducible by hydrogen. It is obtained as a dark-brown precipitate, which becomes nearly black on drying, by passing seleniuretted hydrogen into stannous chloride solution. It dissolves in alkalis and alkaline sulphides (*v.* Uelmann, A. 116, 124).

Stannic selenide $SnSe_2$ is obtained by passing seleniuretted hydrogen into stannic chloride solution, as a yellowish-red precipitate which dries to a brown powder, soluble in caustic alkalis and alkaline sulphides, and forming stannous selenide when heated in hydrogen.

According to Little (A. 112, 213), it is obtained as a tin-white, lustrous, easily-fusible mass, unaffected by hydrochloric acid, but readily decomposed by nitric acid, by heating tin in selenium vapour. Ditte (C. R. 95, 641) describes some double selenides corresponding with the thiostannates (*v. Stannic sulphide*).

Stannous chloride $SnCl_2$ is obtained in the anhydrous condition by heating tin in hydrochloric acid gas, or by heating a mixture of equal weights of 'feathered' (*i.e.* granulated) tin or filings and mercuric chloride, and in monoclinic prisms of the composition $SnCl_2.2H_2O$ (O. Henry, J. Ph. 12, 134) by evaporating a solution of tin in hydrochloric acid. The crystals melt at 40°, and at 100° lose most of their water, together with a little hydrochloric acid. When dried *in vacuo*, or over sulphuric acid, they become anhydrous.

The anhydrous chloride fuses at 249·3° to an oil which boils at 617–628° (Carnelley a. Carleton Williams, C. J. 35, 563), or, according to Biltz and v. Meyer (B. 21, 22), at 606·1°. The anhydrous chloride is sometimes called 'butter of tin,' though that term is usually applied to the hydrated tetrachloride. Stannous chloride is soluble in water and alcohol. On dilution, the aqueous solution becomes turbid, from precipitation, with separation of hydrochloric acid, of a basic chloride $2SnO.HCl.H_2O$, which is also formed when the clear solution is exposed to the air. Mallet (C. J. 1879, 524) has observed a gelatinous deposit of the composition $SnO_2.HCl$, to which he has applied the term *chlor-stannic acid*, in a solution of stannous chloride after long standing. Donath (Rep. Anal. Chem. 7, 77) considers that this body is produced, together with stannic hydroxide, by the action of light on aqueous stannous chloride.

R. Engel (C. R. 106, 1398) has obtained a body of the composition $SnCl_2.HCl.3H_2O$, which he calls *chlorostannic acid*, by passing oxychlorine over the hydrate $SnCl_22H_2O$. The crystals fuse to a clear liquid having the above composition, and depositing, when cooled to $-40°$, slender silky needles which melt at about $-27°$. According to Ditte (C. R. 97, 42), however, the liquid contains a chloride of the composition $SnCl_2.H_2O$, which is also formed by the action of concentrated hydrochloric acid on the chloride $SnCl_2.2H_2O$.

Stannous chloride forms crystalline double chlorides with the alkalis (*v.* Benas, C. C. 1884, 957, forming salts of the composition $SnCl_2.KCl.H_2O$ and $SnCl_2.2KCl.H_2O$). It absorbs dry ammonia, with formation of a body of the composition $SnCl_2.NH_3$.

Stannous chloride is largely used in dyeing and calico-printing under the name 'tin salts' or 'tin crystals.' The use of this salt, or of a mixture of it with stannic chloride, is extremely old, and is said to have been known to Cornelius Drebbel in 1630. A patent was taken out in England as early as 1748 by O. Pawl (Specification No. 630, 1748) for the use of tin dissolved in aquafortis, with addition of ammonium chloride, for dyeing in scarlet.

In making tin salt for these purposes, the tin is dissolved in stone vats in hydrochloric acid free from iron and of 20°Bé. Sometimes the operation is conducted in copper vessels, as the electrolytic action between the metals facilitates solution. No copper enters into solution so long as any tin remains undissolved. The charge is heated gently for twelve hours, and the solution is concentrated to 68°Bé. in copper pans containing pieces of tin to prevent solution of the copper, and is then allowed to crystallise (Chem. Zeit. 9, 851).

The hydrochloric acid is frequently mixed with nitric acid, so that more or less stannic chloride $SnCl_4$ will be present in the solution according to the proposed use of the product. The tin is added in portions, and the liquid is cooled to keep down the production of the stannic salt. A solution consisting of stannic and stannous chloride, obtained by dissolving tin in aqua regia, is used in the preparation of 'fuchsine' under the name 'nitrate of tin' or 'physic.'

A solution consisting of stannic chloride, containing more or less stannous chloride, and used in dyeing under the name 'oxychloride of tin' or 'pink cutting liquid,' is prepared by adding 1 part of stannous chloride to $1\frac{1}{2}$ parts of nitric acid of sp.gr. 1·31 in portions, with constant stirring to prevent boiling over from the violence of the action, or by dissolving 337 parts of stannous chloride in 300 parts of hydrochloric acid (20°Tw.), with the aid of a minimum of water, and adding 58 parts of potassium chlorate in portions.

Stannic chloride $SnCl_4$ is obtained by passing dry chlorine over melted tin, or by heating a mixture of 4 parts of mercuric chloride and 1 of tin filings. The chloride distils over as a colourless mobile liquid, boiling at 113·89° at 760 mm. pressure (Thorpe, C. J. 37, 331), and solidifying at $-33°$ to small white crystals (Besson, C. R. 109, 940).

When exposed to the air, it emits dense white fumes, and is finally converted into a crystalline hydrate $SnCl_4.5H_2O$ (Lewy, C. R. 21, 369), which is also obtained, with evolution of heat, by mixing stannic chloride with one-third its weight of water. This hydrate is sometimes known as 'butter of tin,' or, in dyeing, as 'oxymuriate of tin.' Hydrates of the composition $SnCl_4.3H_2O$ and $SnCl_4.8H_2O$ are also known.

Stannic chloride forms crystalline double chlorides, sometimes called *chloro-stannates*, with the alkaline chlorides; thus, $2KCl.SnCl_4$ and $2NH_4.NH_4Cl.SnCl_4$, the latter forming the 'pink salt' formerly much used by dyers.

It dissolves phosphorus and iodine, and mixes with bromine and carbon bisulphide. It converts mercury into calomel, and is itself decomposed by nitric acid, with precipitation of metastannic acid. Among the bodies produced by direct combination with other compounds may be mentioned $SnCl_4.2NH_3$, a soluble volatile solid (Rose, P. 16, 63); $3SnCl_42PH_3$, a yellow fuming solid (Rose, P. 24, 159); $SnCl_4N_2O_3$, a yellow amorphous mass; $SnCl_4SO_3$, a white solid (Rose, P. 44, 320); $SnCl_4PCl_5$ and $SnCl_4POCl_3$ (Casselmann, A. 83, 257); $SnCl_42C_2H_5HO$, a white crystalline body, and $SnCl_42(C_2H_5)_2O$, a white crystalline body (Coldridge, P. M. [5] 29, 383, 480). A yellow crystalline body $SnCl_4.2SCl_4$, fusing below 30°, is obtained by the action of chlorine on stannic sulphide (Rose, P. 42, 517).

Stannic chloride absorbs large quantities of chlorine at low temperatures, with considerable increase in volume and lowering of the melting-point (Besson, C. R. 109, 940).

Regarding the use of stannic chloride for dyeing and calico-printing, *v. Stannous chloride.*

Tin chlorobromides of the composition $SnCl_3Br$, $SnCl_2Br_2$, and $SnClBr_3$ are known (*v.* Ladenburg, A. 8, 60; and Rayman a. Preis, C. C. 1882, 773).

Stannous bromide $SnBr_2$ is obtained in solution by dissolving tin in hydrobromic acid (Balard, A. Ch. [2] 32, 337). It may be obtained as an anhydrous, pale-yellow, crystalline mass by heating tin in hydrobromic acid vapour and re-distilling the product.

According to Rayman and Preis (A. 223, 323), it melts at 215·5° to a pale-yellow oily liquid, of sp.gr. 5·117 at 17°. According to Carnelley and Carleton Williams (C. J. 35, 564), it melts at 259°, and boils at 617–634°.

A hydrate $SnBr_2.H_2O$ separates in needles or thin plates from the greenish solution of tin in warm concentrated hydrobromic acid. It loses its water in dry air, or when heated to 70–80°. It dissolves in a little water, but is decomposed by excess, with precipitation of a gelatinous precipitate (*v.* Benas, C. C. 1884, 957). A hydrate $SnBr_2.2H_2O$, crystallising in large monoclinic tables, is also obtained from the solution of tin in hydrobromic acid (Benas, *l.c.*).

Benas and Rayman and Preis have also described compounds of stannous bromide with potassium and ammonium bromide.

Stannic bromide $SnBr_4$ was discovered in 1826 by Balard (A. Ch. [2] 32, 337). It is obtained by the action of bromine on tin, preferably, on account of the violence of the action with pure bromine, by gradually adding the tin to a solution of bromine in carbon bisulphide, or by passing the vapour of bromine over heated tin (Carnelley a. O'Shea, C. J. 33, 55).

This compound forms a white iridescent deliquescent mass, which, by distillation, is obtained in small, well-formed, highly lustrous crystals, melting at 30° and boiling at 201° (uncor.) (Carnelley a. O'Shea, *l.c.*), or at 203° (cor.) (Rayman a. Preis, C. C. 1882, 773), and having a sp.gr. of 3·349 at 3·5° (Rayman a. Preis, *l.c.*).

It fumes in the air, and dissolves readily in water. The solution deposits stannic hydroxide on heating or after standing. A hydrate $SnBr_4.4H_2O$ is obtained in colourless transparent fuming crystals, by exposing the anhydrous bromide to moist air, or by dissolving in a little water and evaporating over sulphuric acid. Oxybromides $Sn_3Br_6O.12H_2O$ and $SnBr_8O_2.10H_2O$, obtained from stannic bromide, and a compound $SnBr_4.2NH_3$, obtained by absorption of ammonia by the warmed bromide, are also known (Rayman a. Preis, *l.c.*).

Stannic bromide unites with ether to form a deliquescent crystalline body $SnBr_4.(C_2H_5)_2O$ (Nicklés, C. R. 52, 869). By evaporating solutions of the mixed chlorides, Rayman and Preis (*l.c.*) have obtained the following double bromides: $2NaBr.SnBr_4.6H_2O$, in pale-yellow, soluble crystals; $CaBr_2.SnBr_4.6H_2O$, in slender deliquescent needles; $MgBr_2.SnBr_4.10H_2O$, in pale-yellow, deliquescent tables; $MnBr_2.SnBr_4.6H_2O$, in large, pale-yellow, deliquescent crystals; $FeBr_2.SnBr_4.6H_2O$, in greenish, granular crystals; $NiBr_2.SnBr_4.8H_2O$, in apple-green, granular, deliquescent crystals; and $CoBr_2.SnBr_4.10H_2O$, in yellowish-red, deliquescent tables.

Stannous iodide SnI_2 is obtained by dissolving tin in concentrated hydriodic acid. At the ordinary pressure solution is extremely slow, but it proceeds more rapidly in a sealed tube at 120–150° (Wöhler a. Dünhaupt, A. 86, 374). It may also be obtained in yellowish-red needles, slightly soluble in water and readily soluble in solutions of alkaline chlorides and iodides, and in hydrochloric acid, by addition of potassium iodide in slight excess to a concentrated solution of stannous chloride. The aqueous solution is decomposed by much water, with separation of hydriodic acid and a yellow, insoluble body whose composition varies with the amount of water present (Personne, C. R. 54, 216).

Stannous iodide melts at 316° (Carnelley a. Carleton Williams, C. J. 35, 564) and volatilises at a red heat. It absorbs dry ammonia, with formation of a white body probably having the composition $2NH_3.SnI_2$ (Rammelsberg, P. 48, 169). It unites with other metallic iodides, and with stannous chloride.

Stannic iodide SnI_4 is obtained in yellowish-red octahedra of sp.gr. 4·696 at 11° (Bödeker, Die Beziehung zwischen Dichte und Zusammensetzung, &c., Leipzig, 1860), melting at 146° and boiling at 295° (Personne, J. 15, 172), by heating tin filings, preferably moistened with carbon bisulphide, with iodine to a temperature above 50°.

It dissolves in carbon bisulphide, ether, alcohol, chloroform, and benzene. Water decomposes it into stannic hydroxide and hydriodic acid.

Stannous fluoride SnF_2 is obtained in small, opaque, white, monoclinic tables of sweetish astringent taste, by evaporating a solution of stannous hydroxide in hydrofluoric acid.

Stannic fluoride SnF_4 is not known in the free state, but double fluorides, known as stannofluorides, exist (Marignac, J. 1859, 110). Thus potassium stannofluoride $C_2SnF_6H_2O$ crystallises in thin glistening plates or rhombic pyramids, from a mixture of potassium stannate solution and hydrofluoric acid. From solutions containing excess of hydrofluoric acid, the salt $K_2SnF_6HKF_2$ crystallises out. Many other crystalline stannofluorides are known.

The following is a list of the principal patents taken out for improvements in the preparation of tin salts and oxides:—

J. Greenwood, J. Mercer, and J. Barnes, No. 10,757, 1845 (described previously). J. Young, No. 12,359, 1848, and No. 12,744, 1849 (described previously). T. Rowlandson, No. 12,497, 1849 (obtaining alkaline stannates from tin ore and 'other matters containing tin'). J. Mercer and W. Blythe, No. 12,897, 1849 (obtaining phosphostannate and arseniostannate of sodium). M. J. Roberts, No. 104, 1852 (obtaining stannic oxide by roasting the metal in steam or air). T. Richardson, No. 14,093, 1852 (obtaining sodium stannate from the oxide of tin obtained in softening the 'hard lead of commerce'). E. Haeffely, No. 603, 1854 (described previously). J. Higgin, No. 766, 1854 (obtaining stannous and stannic chloride, stannic oxide, and stannates from scrap tin &c.). J. Dale, No. 2,122, 1855 (oxidising proto-salts of tin with the nitrous fumes obtained in the manufacture of arsenic acid; also obtaining the oxide and stannates). C. F. Claus, No. 57, 1857 (obtaining chloride and oxide from scrap tin). T. Roberts and J. Dale, No. 2,242, 1858 (obtaining sodium stannate from the metal by the action of soda and sodium nitrite). T. Cobley, No. 1,776, 1861 (obtaining tin silicofluoride). E. Powers and J. G. Dale, No. 91, 1863 (obtaining stannates from the ore or metal). J. J. Marçais, No. 1,442, 1866 (obtaining stannous chloride from the oxide). O. Ott, No. 890, 1871 (obtaining stannous chloride and oxide from tin waste). E. P. H. Vaughan (communicated by L. Lennig), No. 2,269, 1871 (obtaining alkaline stannates from scrap tin, &c.). J. E. T. Woods, No. 277, 1872 (furnace for making stannates). F. G. Morton, Nos. 1,739 and 3,676, 1872 (obtaining stannous chloride from scrap tin, &c.). A. Gutensohn, No. 258, 1873 (the same). J. Stuart, No. 1,276, 1874 (the same). C. H. Silber (communicated by L. Gonin), No. 3,064, 1875 (obtaining tin oleate). E. A. Parnell, No. 3,183, 1876 (obtaining tin oxide from scrap tin). A. P. Price, No. 2,119, 1884 (obtaining sodium stannate from scrap tin). H. J. Haddan (communicated by A. Lambotte), No. 14,672, 1884 (obtaining stannic chloride from waste tin plate by the action of chlorine).

H. H. Lake (communicated by Wirth & Co.), No. 10,018, 1885 (obtaining stannous chloride by the action of hydrochloric acid gas on scrap tin at elevated temperatures). J. J. Hood and A. G. Salamon, No. 12,110, 1886 (preparing and purifying metastannic acid). J. Bang and A. Ruffin, No. 70, 1890 (obtaining metastannic acid or sodium stannate from scrap tin &c.).

TINCAL. *Crude borax v.* Boron; also *Sodium biborate*, art. Sodium.

TIN MORDANTS *v.* Dyeing.

TIN PLATES *v.* Tin.

TIN PYRITES. *Stannine, tin sulphide, bell metal ore* $Cu_2(Fe.Zn)SnS_4$. A sulpho-stannate of copper and iron, occasionally containing zinc, found in Cornwall, and to a small extent in Ireland; also at Zinnwald in Bohemia. Crystallises in forms derived from the regular systems. Opaque; colour, steel grey, but frequently yellowish from intermixture of copper pyrites. H = 4, sp.gr. 4·3–4·5. On charcoal before the blow-pipe melts to grey brittle bead, containing copper and iron, and surrounded by a white sublimate of stannic oxide. Easily decomposed by nitric acid, forming a blue solution, with separation of sulphur and stannic oxide.

TIN SALTS or **TIN CRYSTALS** (*Stannous chloride*) *v. Tin salts and oxides*, art. Tin.

TIN STONE (*Native oxide of tin*) *v. Tin salts and oxides*, art. Tin.

TINTOMETER *v.* Colorimeter.

TIN WHITE COBALT. *Smaltine, Arsenide of cobalt v.* Cobalt.

TITANITE *v.* Titanium.

TITANIUM. Sym., Ti. At. wt. 48·01 (Thorpe).

Titanium is not found in the free state, but occurs as oxide in three minerals of different crystalline form: *rutile*, *anatase*, and *brookite*. It is found as *titaniferous iron ore* or *ilmenite* $(FeTi)_2O_3$, and in smaller quantities as *sphene* or *titanite* $CaTiSiO_5$, *perofskite* $(CaFe)TiO_3$, and *schorlomite* $Ca(TiFe)SiO_5$. It occurs in magnetic iron ores, and is thus frequently found in slags and pig iron; and in other minerals, in soils, clays, certain mineral waters, and in the sun's atmosphere. The presence of titanium oxide in clays considerably reduces their refractibility. Titanium is said to be diffused throughout all primitive granite rocks (Dieulafait).

Titanium is a dark-grey amorphous powder of iron-grey lustre. When heated in air it ignites with a vivid flash, with formation of the oxide and some nitride. When heated with red lead it ignites with detonation. It decomposes boiling water, is soluble in dilute acids, and combines with chlorine at high temperatures.

Titanium resembles tin in its liquid volatile tetrachloride and acid forming dioxide, but in forming a sesquioxide and the corresponding compounds it resembles iron.

Four oxides are known, TiO, Ti_2O_3, TiO_2, and TiO_3, and several titanic acids and titanates corresponding to the dioxide.

Among the compounds of titanium may be mentioned: three chlorides, $TiCl_2$, Ti_2Cl_6, $TiCl_4$, a tetrabromide, tetriodide, tetrafluoride, titanofluorides of the alkalis and alkaline earths, three sulphides, TiS, Ti_2S_3, and TiS_2, and three nitrides.

TITANIUM GREEN. Titanium ferrocyanide, prepared by adding potassium ferrocyanide to a solution of hydrated titanic oxide in hydrochloric acid, has been suggested as a substitute for Schweinfurth green and other arsenical pigments (Elsner, D. P. J. 905, 130; Gentele, D. P. J. 140, 238).

TITRATION *v.* Analysis.

TIZA. A name for boronatrocalcite, found in the nitrate of soda deposits in South America.

TOAD'S EYE (*Native oxide of tin*) *v. Tin salts and oxides*, art. Tin.

TOBACCO. Tobacco is the name given to the dried leaves of the various species of the genus *Nicotiana*, of the order *Solanaceæ*, and is said to be derived from the word *tobaco*, or *tabac*, the name of the instrument in which the natives of America smoked the leaves. Of the various species, *Nicotiana Tabacum* is by far the most extensively cultivated. It is a fine plant, and grows to the height of 6 or 7 feet, with large oblong leaves, which embrace the stem at their base, and with a pink flower. It constitutes a very large proportion of the tobacco of commerce, and is grown nearly all over the world. American tobacco is almost exclusively of this species, although there are many varieties of it, such as Kentucky, Big Frederick, Virginian, Maryland, and probably Havannah. The next species in importance is *Nicotiana rustica* or Syrian tobacco. It is a comparatively small plant, with a stem about 3 or 4 feet in height, to which the leaves are attached by stalks, and its flower is green. It furnishes the Turkish, Syrian, and probably the Latakia tobacco of commerce. It is a native of America, but is grown chiefly in Asia, Africa, and Europe. It is a hardier plant than the preceding, of quicker growth and earlier maturity, and in the dry state is sometimes green. The third important species is *Nicotiana persica*, or Shiraz tobacco. It is a native of Persia, with oblong stem-leaves, and its flower is white. There are other species, and many varieties of the plant of less importance.

The use of tobacco for smoking and chewing purposes is supposed to have been originated by the North American Indians at a very early period. When America was first discovered, and afterwards when fresh portions of the country were explored, the practice was found to be prevalent among all the tribes. Its introduction into Europe very soon followed. The plant was first cultivated in Spain, afterwards introduced into Italy in 1560, and into France at about the same period. Sir John Hawkins is stated to be the first to have brought the plant into England in 1565. The custom of smoking it quickly succeeded its introduction, and the growth of the habit in spite of the immense amount of opposition of all kinds is a very remarkable circumstance. Nearly the whole of the early literature on the subject was written antagonistically. Kings' 'counterblasts,' Popes' anathemas, Sultans' decrees, laws, orders, violent punishments &c., proved of no avail. Plantations sprang up, and when the use of tobacco was found by taxation to yield a fair amount of revenue, the princely deprecations became more modified and finally ceased. In England the custom is still growing, the annual consumption per head of population being 11·7 ounces in 1821, 16·3 ounces in 1851, 22·3 ounces in 1881, and close upon 26 ounces in 1891.

The tobacco plant contains a large number of the organic constituents common to the vegetable kingdom, amongst which may be mentioned cellulose, starch, albuminoids, glucosides, gums, chlorophyll, and many organic acids, but the characteristic organic constituent of the plant is the alkaloid *nicotine*, with which is generally associated the essential oil, or *tobacco camphor*, as it is called, viz. *nicotianin*. It is on the proportions which all these organic substances bear to one another in the plant that the aroma and the taste of the tobacco depend. The burning property is also influenced somewhat by them, but it is likewise very much affected by the quantity and the quality of the mineral constituents. The freshly-cut green leaves contain between 85 and 90 p.c. of water, and when dry contain roughly, according to Flückiger, cellulose 7 to 8 p.c.; albuminoids, 15 to 25 p.c.; gum, 4 to 6 p.c.; resin and fatty substances, 2 to 6 p.c.; and starch 3 to 6 p.c. The nicotine varies in different kinds of tobacco from 1 to 9 p.c. Syrian tobacco contains about 1 or 2, Havannah and Manilla 2 to 3, Virginian and Kentucky up to 7, while other kinds, such as French, sometimes contain as much as 9 p.c. The nicotianin is said to be present in very small quantity, only 11 grains being reported as obtained in one case from 6 pounds of tobacco. It is supposed that the aroma depends largely on the presence of this substance, and it is believed that the conditions of soil and climate which are conducive to its production are precisely those which are unfavourable to the production of nicotine. It is quite clear that the good quality of a tobacco is not dependent on the high percentage of nicotine present, as the most delicately-flavoured varieties are those which contain only a small quantity of it. The cellulose, albuminoids, gums, &c., give off objectionable odours on burning, and it is the process of fermentation which gets rid of or modifies some of these bodies when present in considerable quantity. The fermentation, on the other hand, should not be excessive, as ammoniacal salts are thereby produced, which are objectionable. Some of the tropically grown varieties contain little of these prejudicial substances, and, as a result, fermentation is less extensively necessary, and sun-drying is very often sufficient. The organic acids in tobacco are chiefly malic, citric, oxalic, pectic, and sometimes acetic, but the last has only been found in fermented leaves.

The following analyses have been selected from the United States Statistics for Agriculture (1880). They show a wide variation, and illustrate the difficulty of laying down anything like a definite composition for tobacco.

Percentage composition of American tobacco (*dried at* 100°C.)

——	1	2	3	4	5	6	7	8	9
Nicotine	3·26	4·30	5·29	3·12	4·32	4·25	4·06	1·14	1·04
Resin and fatty substances . .	4·15	4·65	4·99	5·34	6·28	7·26	4·29	2·93	4·02
Starch	5·89	2·75	3·54	4·15	2·45	2·79	3·22	3·14	3·67
Glucose	6·89	2·75	0·00	0·00	0·00	0·00	0·00	0·00	0·00
Albuminoids (N × 6·25) . . .	16·09	13·66	16·54	15·98	15·80	16·50	18·09	17·33	14·62
Pectic acid (anhydride) . . .	6·19	7·46	6·01	7·49	6·66	7·43	6·29	11·24	12·59
Citric „ „ . . .	2·12	2·84	2·99	4·05	1·18	4·31	5·80	4·95	1·61
Malic „ „ . . .	5·02	7·58	5·51	9·26	3·94	7·90	10·09	5·04	5·46
Oxalic „ „ . . .	0·84	1·03	1·30	2·18	3·49	2·06	0·92	0·95	0·94
Acetic „ „ . . .	0·42	0·55	0·39	0·64	1·62	0·28	0·31	0·48	0·57
Nitric „ „ . . .	0·00	0·00	1·55	0·00	0·00	1·65	3·23	2·39	0·00
Ammonia . . .	0·33	0·32	0·98	0·48	0·76	1·65	0·65	0·62	0·22
Cellulose (crude fibre) . . .	9·58	9·24	9·68	12·18	9·08	8·30	10·61	15·23	15·12
Sand	0·55	2·38	2·25	0·66	4·17	0·76	1·34	1·48	1·64
Ash, exclusive of sand and carbonic anhydride	12·41	13·36	14·37	16·06	13·30	15·54	15·10	18·56	17·98
Undetermined	26·26	27·13	24·61	18·11	26·95	19·32	16·00	14·52	20·52
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

In the above table the analyses are of the following varieties of tobacco:—

1. Virginia, uncured; for manufacturing plug tobacco.

2. Virginia, fire-cured; for the German and Continental trade; low grade.

3. Tennessee, Clarksville; fire-cured; gummy, for the German and English markets. Soil: heavy rich loam.

4. Kentucky, Mason county; air-cured; for cutting or plug tobacco.

5. Louisiana, ‘Perique’ tobacco; ‘cured in its juices.’

6. Louisiana, ‘Perique’ tobacco; air-cured.

7. Connecticut seed-leaf, New Milford. Soil: rich loam.

8. Connecticut seed-leaf, Hartford. Sandy soil.

9. Pennsylvania seed-leaf, Lancaster county.

The ash of tobacco varies in quantity, but is generally between 12 and 20 p.c. of the dried sample, and it is on its composition that the burning qualities of tobacco so largely depend. It invariably contains potash, soda, lime, magnesia, alumina, iron oxide (trace), carbonic, silicic, phosphoric, and sulphuric acids, and chlorine. The potash may be present to the extent of 30 p.c. of the total ash, and in the tobacco should be mainly combined with the organic acids. It is considered that the ready decomposition of these organic potash salts by heat constitutes a good burning tobacco. Potassium nitrate also assists in the burning, and is often added to inferior material, but it is not essential, and some of the best varieties of tobacco contain little or none of it. The potash salts are converted into carbonate by burning; consequently, the combined presence of potash and carbonic acid in quantity in the ash is a good indication. From the excess of these two constituents the others should be present in small quantities, the lime generally lower than the potash, and smaller quantities of soda, magnesia, and alumina. Iron is objectionable, as giving a red ash. Silicic and phosphoric acids may be present to a considerable extent without detriment to combustion, but sulphates do not assist combustion, and chlorine, unless present in small amount, retards it. The leaves of tobacco contain more lime, magnesia, and silicic acid, and less alkali, phosphoric acid, and chlorine than the stalks; and potassium nitrate, which is not present in fresh leaves but only in dry, also predominates in the stalks and is present even in the green stalks and veins. From these causes the stalks burn more readily than the leaves, and it is their presence in the so-called 'bird's-eye' tobacco, when saltpetre is not surreptitiously added, which renders that tobacco so easily combustible and hot.

Many analyses of the ash of tobacco have appeared. The following are examples of American varieties:—

Percentage Composition of Ash, exclusive of Sand and Carbonic Acid.

—	1	2	3	4
Total ash in dried leaves	14·29	17·42	19·21	21·85
Ash exclusive of sand and CO_2	12·41	13·36	14·37	16·06
Analyses.				
Potash	34·16	26·55	33·15	39·51
Soda	0·26	0·22	0·15	0·86
Lime	31·76	36·96	36·48	39·80
Magnesia	7·91	11·51	11·85	5·34
Ferric oxide	0·58	0·95	0·51	1·56
Alumina	1·22	1·81	0·95	0·51
Manganous oxide	0·00	0·00	0·25	0·13
Phosphoric anhydride	3·81	3·23	4·42	6·09
Sulphuric ,,	4·99	4·27	6·16	4·52
Silicic ,,	1·39	3·29	3·42	1·20
Chlorine	13·92	11·21	2·66	0·48
	100·00	100·00	100·00	100·00

The numbers of these analyses correspond to the same varieties as those in the previous table of the complete analyses of the dried American tobaccos.

The forms in which tobacco is imported into this country are many and various. There are numerous kinds in the market, each with its own name or brand, but the manufacturer generally buys his material according to its suitability for the purpose for which he requires it. Commercial tobacco, as a rule, is classified under five heads—common, middling, good, fine, and selected—but of course each manufacturer can have his own particular method of assortment. Tobacco is not purchased merely upon its belonging to one of the above classes. Thus one tobacco may be chosen simply for its colour, another for its aroma, another for body, another for its drinking power—that is, its power of absorbing and retaining moisture without becoming too wet; again, a 'fiery' tobacco, containing a considerable amount of potassium nitrate, may be chosen to mix with other material difficult of burning, while a tobacco like Chinese—a very light yellow material, nearly white in colour, without body, and almost flavourless—may be selected entirely for producing variety of colour in mixtures. The following are some of the chief imported varieties:—Virginia, Kentucky, Maryland, Western leaf and strips, Indiana, &c.; Java, Japan, China, Ceylon, Turkish, and German. Some of these come over in the full leaf, some with the mid-ribs removed; these latter are known as 'strips.' Most of them arrive in hogsheads, in which they have been packed in bunches of ten or a dozen leaves tied round with another one, or packed indiscriminately; while some of the more tender varieties, such as Turkish, Chinese, and Ceylon, have been carefully packed leaf upon leaf.

Imported tobaccos, although apparently quite dry and very crisp and brittle, generally contain from 10 to 20 p.c. of water, and on the average about 14 p.c. Very few commodities of commerce are subject to so many requirements as tobacco, and especially is this the case with those kinds used for cigar-making. Leaves for such a purpose must be of a good colour and fair body, possess a pleasant aroma, emit an agreeable odour on burning, have a fairly fine texture, a certain amount of toughness, the ribs and veins must be small, and last, but not least, the material must burn well. The burning test for a cigar tobacco is to ascertain whether the leaf will continue to smoulder after it is once lighted. Cigars are sometimes made of leaves that will not stand this test, in which case a quantity of fiery tobacco is generally mixed in with them, but, needless to say, these are inferior articles, and, unless very carefully made, do not burn evenly.

In the manufacture of cigars the leaves are first moistened with water, opened, stripped of the mid-rib, smoothed, and sorted, the perfect half-leaves being put on one side to be used as wrappers. A fairly good strip is taken and cut into the shape of a balloon gore, fragments and cuttings of the leaf, called the 'fillers,' are placed near one end, and the strip is wrapped round them. Over this is then wound spirally a long narrow rectangular slip, called the wrapper, commencing with the open end and finishing at the pointed or mouth end. The cigars are then gauged, and cut to length, partially dried, and packed. Great dexterity is necessary in making cigars, especially in manipulating the shape and keeping them to size and weight, as well as in evenly packing. Good cigars should be made of the one kind of leaf, but in the common kinds the interior very often consists of a mixture, and sometimes very inferior material is got rid of in this way, care being always taken to conceal it in an attractive wrapper. It has been found that in some cases of foreign-made cigars the wrapper has contained a considerable quantity of saltpetre, while the interior, consisting of the same tobacco, has none. This would seem to show that saltpetre had been purposely added to render the former more combustible, so as to burn down evenly with the other part.

The bulk of the imported leaves, however, is used for the manufacture of smoking tobaccos. Of these there are two classes—the cut, and the twist or cake tobacco—with various kinds belonging to each. All manners of mixtures of the various brands of leaves are used in making these. The imported tobacco is moistened with water, and covered over with cloths until the whole has become sufficiently damp and flaccid to allow the leaves to be easily opened. Steaming facilitates this operation, after which the material is chosen, and treated according to the variety of saleable tobacco required. Shag is generally made from the stronger varieties. The leaves are stripped as in the case of cigars, and sprinkled with sauce, which should be only water, but to which salt is sometimes added. They are then placed in a square iron box, and pressed into a cake. During this operation, the excess of the water or 'liquor,' deeply coloured with extractive, is squeezed out. This is sometimes used as sauce for mixing with other kinds of tobacco, and is occasionally sold as a sheep-wash and as an insect-destroyer. The cake is then submitted to the action of a mechanical cutting machine, somewhat similar to a paper-cutting machine, with an adjustable feed, by which it is cut into shreds of the desired fineness. These cuttings are submitted to a gentle heat, pulled, mixed, and, with the desired amount of moisture present, are sent into the market. 'Bird's-eye' is prepared in a somewhat similar manner, but the mid-ribs of the leaves are not removed. It is from the fancied resemblance of the cross-sections of these mid-ribs to the eyes of birds that the name has originated. 'Returns' is made up of the broken pieces of leaves and the siftings from the various processes of manufacture. There are many other varieties of cut tobacco, with all kinds of fanciful names; some are simple tobaccos, and some are very complex mixtures, the choice of this, and also of the name, depending entirely on the will of the manufacturer. In some coarse-cut mixtures the different kinds of tobacco present can readily be discerned--the light-yellow shreds being Chinese, the black generally cut Cavendish, while the intermediate coloured shreds can be traced to the American tobaccos. These mixtures are sometimes scented to improve their aroma, although, of course, the scent is entirely lost in smoking. Neroli oil, or oil of orange-flower, mixed with alcohol is often used for this purpose.

Twist or cake tobacco is made by stripping the leaves, placing them end to end, and twisting or spinning them into ropes of varying thickness, either by hand or by a spinning wheel. The rope so obtained is then coiled round a reel, or wound into a ball, and the whole is steeped in 'liquor,' pressed and oiled with sweet oil. Pigtail, Bogie, Negrohead, and other rolls are produced in this way, the chief difference between them being in the thickness of the rope. It was in these tobaccos, especially the thicker varieties, that a large amount of water used to be got rid of, the quantity present often being between 40 and 50 p.c. The darkest and strongest kinds of leaves are usually employed in this branch of manufacture, as also in the preparation of Cavendish or cake tobacco. To prepare the latter, the leaves are generally sprinkled with a liquor, or infusion of leaves and stalks, allowed to ferment, during which process the colour darkens, and then placed in heaps and squeezed into small cakes. All these varieties of twist are darker and stronger than the ordinary cut tobaccos. In America milder forms of cake are made, and it is often the custom to prepare them for the purpose of chewing by previously saturating the leaves with liquorice or molasses, but in England this is illegal, as also is the sale of such tobacco.

Cigarettes are generally made of the fine-cut Syrian species of tobacco, such as Turkish, Salonica, &c., which are mild and of little, though agreeable, flavour. Recently American tobacco has been employed in this manufacture, and with a certain amount of success.

Snuff is made almost entirely of the stalks and mid-ribs of tobacco, but a little of the finest parts of the leaf is sometimes worked in. It is sold in two forms, dry and moist, and the difference in quality is dependent on the flavour, the pungency, and the scent. The dry snuffs are, as a rule, more finely ground than the moist, and they comprise the well-known Welsh, Scotch, and Irish varieties; while the moist snuffs include most of the prepared kinds with fanciful names. The stalks are cut into small pieces, moistened with water—sometimes lime-water—and allowed to ferment, frequently for months. They are then ground to the requisite degree of fineness in an iron mortar, with a pestle to which a rotary and grinding motion is given. The material is dried and flavoured for Scotch snuff. For Irish and Welsh snuffs, the stalks, previous to grinding, are gently roasted, by which the characteristic smell of these varieties is produced. The stalks are ground wet for moist snuffs in a kind of grindstone mill, and the material is kept moist and fermented after this operation. The depth of colour depends on the degree to which the fermentation is carried. With the fermented material is then mixed salt, sal-ammoniac, lime-water, or the other alkaline salts allowed by the Excise, and the mixture is scented, moistened to the right degree, well mixed, rubbed through a sieve, and sent into the market. Salt is supposed to preserve snuff from mouldiness and to assist it in retaining moisture, while the sal-ammoniac &c. add to its pungency. The moisture should be about 25 p.c., but very often it is as much as between 40 and 50 p.c. The scents used for this purpose are generally otto of roses, oil of bergamot, orris root, or lavender; or mixtures of these. Snuffs, and moist snuffs especially, are very liable to adulteration. Amongst other things the following have been found present: oxides of iron, red lead, chromate of lead, and chromate of potash as colouring materials; carbonate of potash, chalk, alkaline and earthy phosphates, sulphates, excess of salt, lime, &c. as diluents; and some snuffs have been found to be quite free from the tobacco plant.

All kinds of vegetable matter have been used for the adulteration of tobacco, amongst the most frequently found substances being dock, rhubarb, coltsfoot, cabbage, potato, oak, elm, endive, chicory, hay, wheat, gum, &c.; saccharine matters, such as treacle, liquorice, honey, &c.; while there are a host of mineral adulterants, viz. salt, sal-ammoniac, nitrates, carbonates, and sulphates of the alkalis and alkaline earths, yellow ochre, umber, sand, copperas, &c. Glycerin has also been found in tobacco—added, probably, to assist it in retaining moisture. By recent legislation, when the duty on imported tobacco was slightly reduced—in 1887—the amount of water permissible in manufactured tobaccos of all kinds was restricted to 35 p.c. of the total weight, dried at 100°C.; consequently, any water present over and above this amount is, at the present time, an adulterant. Cigars, as a rule, are rarely adulterated with foreign material. They are very often not what their outside appearance would represent them to be, but the interior is generally tobacco, although possibly of a very inferior kind. Cases have been known of cigars containing hay and brown paper, but these are rare. The chief imposition in respect to cigars seems to be the practice of placing home-made articles in imitation foreign boxes. Another custom is to send Continental cigars out to the West Indies, trans-ship, repack them if necessary, and send them back again as a special brand.

Tobacco is analysed, as regards its organic and inorganic constituents, by the usual methods described in many books on agricultural and quantitative analysis. It will suffice here to describe the method for the estimation of the nicotine. Twenty grms. of the tobacco are digested with 100 c.c. of alcohol (3 vols. of ·830 alcohol to 2 vols. of water), or dilute sulphuric acid may be substituted for this; water is then added, and the solution is filtered through muslin, rendered alkaline with potash, or preferably lime, and distilled in steam. The distillate is neutralised with oxalic acid, evaporated to dryness, and the residue washed with water-free ether, in which nicotine oxalate is insoluble. A solution of potash is then added to the residue, and the liquid shaken with ether and separated. The ethereal solution of free nicotine is evaporated spontaneously, or by the aid of very little heat, water added, and the base estimated by titration with standard sulphuric acid, using litmus as the indicator; 1 c.c. decinormal sulphuric acid is equivalent to ·00324 grm. of nicotine.

ENGLISH-GROWN TOBACCO.

In 1886, owing to the agricultural depression in this country, the question of cultivating the plant at home was raised, and permission was obtained, with rather severe restrictions, to make experiments on the subject. So promising were the results that permission, with modified restrictions, was again obtained in 1887, and the further experiments were so successful as regards the crop that the question of a new industry in the country was seriously discussed. It was deemed certain that with very slight assistance from the Government, in the shape of a little concession of duty, the country would have been relieved from its embarrassed agricultural position. Such a thing, however, was not entertained by the authorities, and the whole idea of cultivation met with so much opposition, interested and otherwise, that the scheme wavered, and has, for the time being, become dormant. It was certainly proved that tobacco could be grown in this country as a farm crop, although it was not to be expected that the best Havannah leaves could be grown here, any more than they could be cultivated in Germany or Kentucky. The manufactured tobacco which was obtained was hardly a fair test of what might be done, on account of the insufficiency of experiments in the curing and fermentation, each variety of the plant, as is well known, requiring its own special method of treatment. This part of the subject was never fully examined, and, in fact, was scarcely entered into at all in a practical sense. The whole thing was prematurely condemned.[1]

A chemical examination of some specimens grown in the cretaceous soils of Kent showed that the ground had been heavily, and to some extent improperly, manured. On the next page are some analyses of the ash of these tobaccos made by Arthur Wingham.[2]

In the analyses Nos. 1 and 2 are the results obtained with tobacco grown at Faversham, by Lord Harris; Nos. 3 and 4 at Sittingbourne, by C. de L. Faunce de Laune; and No. 5 at East Malling, by W. L. Wigan.

Some English tobacco was examined for nicotine, and the following figures were reported by J. A. Voelcker:—

Light variety,	3·62 p.c.	of nicotine
Dark „	2·41 „	„

A comparison of these ash analyses with those of the American tobaccos will indicate the discrepancies of the former, due in part to incorrect manuring and partly to natural deficiencies of the soil. Common salt and kainit were largely used as manure in the English experiments. These materials should not be used, on account of the chlorine in them. Fertilisers should be carefully chosen, in accordance with the previously-mentioned facts. If potash is wanted in the soil, the sulphate should be employed in preference to the chloride. In America, where the soil is a calcareous one and the tobacco contains little potash, the leaves are sometimes sprinkled with a solution of citrate or acetate of potash to remedy the defect.

The tobacco plant is a most voracious one for mineral matters, and will take up almost anything from the soil; by heavy manuring it may be forced to an extraordinary extent. This

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[1] *Vide* Journal of the Royal Agricultural Society of England, vol. xxiii. part i. Tobacco as a Farm Crop for England, by C. de L. Faunce de Laune.

[2] Ibid. Also S. C. I. 1887, pp. 76, 162, 400 *et seq.* English-grown Tobacco, by Arthur Wingham.

Percentage Composition of Ash.

	1	2	3	4	5
Total ash in dried leaves	25·28	21·19	24·35	23·23	17·03
Analyses.					
Potash	8·02	7·38	9·52	10·14	11·32
Soda	4·42	4·45	3·98	2·40	0·91
Lime	41·02	43·16	37·59	39·22	35·83
Magnesia	3·96	3·92	3·48	3·85	3·49
Iron oxide and alumina	Nil	Nil	0·68	·56	0·70
Phosphoric anhydride	2·64	2·86	3·24	2·14	5·25
Sulphuric anhydride	4·95	4·55	5·61	8·58	5·82
Silica	1·43	1·89	6·13	8·41	6·51
Chlorine	28·02	28·52	9·15	8·42	9·68
Carbonic anhydride (by diff.)	11·85	9·69	22·68	18·18	22·67
	106·31	106·42	102·06	101·90	102·18
Deduct oxygen equiv. for chlorine	6·31	6·42	2·06	1·90	2·18
	100·00	100·00	100·00	100·00	100·00

draining of the soil, no doubt, is the origin of the idea that the tobacco plant poisons the land, since cases have been known of inability to grow anything after a crop of tobacco. The plant is essentially a tropical one, but it can be readily grown in temperate climates. The soil should be, by preference, an alluvial or a light sandy one, and should be rather rich in potash. The operations in the cultivation of tobacco vary, of necessity, according to the country in which it is grown, and also to local fluctuations in climate. The seed-bed should be a light friable soil, well broken up some months before sowing, and with a drain running round it. A brush-heap is usually first burnt over the ground, to kill weeds and supply potash. The seeds are mixed with wood ashes, and sown towards the middle of March or April, according as the spring is early or late. In cold climates, such as England, the seeds are sown in hot-beds. The seed-bed is covered, after the seeds have been sown, with a manure and a sprinkling of ashes, and finally with cut straw or small branches of trees, to protect the seedlings from cold. In India protection from sun and rain is necessary, and this is procured by erecting an awning of straw, leaves, or cloth on sticks a few feet above the ground. The soil is kept moist, but not wet, and the plants, which appear in about a week, require frequent but gentle watering. In two or three weeks they are thinned out, and in seven or eight are transplanted, generally when there are five or six leaves on them, exclusive of seminal leaves. This, as a rule, is done in June and in wet weather. The land is previously ploughed several times and ridged. The ridges are flattened at the top, and the seedlings placed in small hollows on the ridges, a sufficient distance apart—about three feet—to allow room for growth. The transplanting is done in the evening or at night, except in cloudy weather, when it is carried on in the daytime. If the weather is dry, the plants are carefully watered, night and morning, until circumstances render this unnecessary. The plants rapidly shoot up, and are watched carefully for insects.

The grower generally classifies his leaves into three sorts, viz. strong, medium, and mild. The first of these consists of the leaves nearest the roots, the second those in the middle, and the mild ones are at the top of the plant. When the flower first shoots it is nipped off, so that all the nutrition may go to the leaves. This topping, as it is called, is not done in Turkey and some Eastern countries, where small leaves are required, and where, sometimes, the leaves, buds, and flowers are all used. The number of leaves on a plant may be regulated, according to the quality desired, by nipping the stem earlier. Thus a plant may be made to yield eight or ten leaves of a strong flavour, or a few more of a medium flavour, or still more of a mild kind. Suckers appear, after nipping the plant, at the junction of the leaves and the stem, and these are removed as quickly and completely as possible, since they grow very rapidly, and to a considerable length, and drain the plant of all its nourishment. The harvest generally takes place in August or the beginning of September, and the methods of cutting are various. Some planters aim at a uniform quality of leaf by cutting a few leaves from the plant nearest the roots, leaving it eight or ten days for the other leaves to strengthen, then cutting a few more leaves, and so on. Others cut the stems close to the ground, and leave the whole plant to dry in the sun. The best method, however, especially if the stems are large, appears to be to split the stems nearly to the bottom after cutting, and to hang the plants on sticks to dry.

The drying, curing, and fermenting of the leaves are processes the nature of which depends entirely upon locality. Thus in India, Ceylon, and some Eastern countries the leaves are simply sun-dried, and sent into the market. In Europe they are artificially dried, while in America both natural and artificial methods are employed. In some parts they are hung till the spring, and then bulked; in others they are dried in the drying-house, placed in heaps and covered over, and left for a week or two to ferment, with occasional turning over to prevent excessive fermentation and spontaneous firing. When fermentation is complete the leaves are sorted, partly dried, and packed under pressure in barrels or hogsheads. A variety of opinion exists as to the best temperature for artificial drying, but 70°F., with a maximum of 90°, seems to be that usually aimed at.

The colour of the dried leaves is governed very much by the details of drying. Thus a fresh leaf subjected at once to a high temperature and dried rapidly will be green, while a gradually dried one will assume a light-brown colour. The colours change during slow drying, and the leaves may acquire a light-yellow, varying to a darker yellow or light-brown tint, and thence vary in shade to the darkest brown. It is possible to fix these colours at any desired shade, and this art of fixing, in connection with large quantities of material, is one of considerable financial importance, since the colour takes a prominent position in the commercial value of the leaf.

Sir Walter Raleigh is generally credited with the distinction of being the first to introduce the cultivation of tobacco into the British Isles in 1586, although he did not bring over the first specimens. From the beginning its cultivation was successful, but it was prohibited by James I. and Charles I., although with little effect. When the imported article was made a source of revenue, the home-grown tobacco was heavily taxed, as it was hoped this would lead to the abandonment of its cultivation through want of profit; this action being taken on account of the difficulty of collecting the duty, and because of the chances of fraud on the revenue in connection with the native material. This suspected evasion of duty took place extensively, and in 1652 the cultivation was prohibited in England, the plantations being afterwards ordered to be destroyed. The surreptitious growth, however, continued, and it was not until the reign of George III., by an Act passed in 1782, that the cultivation could be finally stopped, and what might have been a profitable industry was forcibly driven out of the country. The Yorkshire plantations were by this Act destroyed, and the planters fined and imprisoned—30,000*l.* being paid as penalties. The growth in Ireland, where it had not been so harshly dealt with, was not suppressed until 1831.

The present annual revenue from tobacco to the United Kingdom is close upon ten millions sterling. Consequently, any scheme which would in any way tend to a re-arrangement of the machinery of the body whose function it is to collect this sum would naturally be strenuously opposed by the officials most concerned. The amount of duty paid is out of all proportion to the actual value of the commodity; thus, it is ten times the value of the inferior qualities of imported leaf, and three times that of the best kinds. The largest quantity of tobacco is imported from the United States, and a considerable amount from Germany, with smaller quantities from Japan, India, China, and other Eastern countries. Cigars are chiefly brought from the West Indies, Philippine Islands, Germany, and, of recent years, Mexico. The manufacture of snuff not increasing simultaneously with the consumption of tooacco, large amounts of stalks, which are not used by the manufacturers, enter this country, and are duty paid as tobacco. These are returned to the Customs officials, and by them destroyed or buried at sea, and it is usual to allow a rebate of duty on them. A. W.

TOBACCO-SEED OIL. Tobacco seeds yield on pressing about 30 p.c. of a greenish-yellow, mild, and odourless oil, sp.gr. 0·923 at 15°, solidifying at −25°, which quickly dries when exposed to the air.

TOLENE *v. Tolu*, art. Balsams.

TOLIDENE (*Orthotolidene*) *v.* Diphenyl.

TOLU *v.* Balsams.

TOLUENE. *Toluol, Methylbenzene* $C_7H_8 = C_6H_5.CH_3$. First discovered by Pelletier and Walter (A. Ch. [2] 67, 278) among the by-products from the manufacture of illuminating gas from the resin of *Pinus maritima*, and named by them *retinaphtha*. Mansfield found it in coal-tar, Cahours and Völkel in wood-spirit and wood-tar, and De la Rue and H. Müller in Rangoon tar. Fittig and Tollens prepared it by the action of sodium on a mixture of brombenzene and methyl iodide in ethereal solution, and thus proved that it was methylbenzene.

The toluene of commerce is obtained from coal-tar by rectification of the fraction boiling between 100 and 120°.

Colourless liquid, boiling at 111°. Does not solidify at −20°. Sp.gr. 0·8824 at 0°, 0·8720 at 15°, 0·8650 at 20°. In its solubilities and solvent powers it closely resembles benzene.

Oxidising agents, such as chromic acid or dilute nitric acid, convert it into benzoic acid; but by treatment, first with chromyl chloride and afterwards with water, it yields benzaldehyde. When the vapour of toluene is passed through a red-hot tube, benzene, anthracene, phenanthrene, dibenzyl, and other hydrocarbons are formed (Berthelot, Bl. 7, 218; Graebe, B. 7, 48). By passing a mixture of the vapours of toluene and benzene through a red-hot tube, Carnelley obtained a highly complex mixture of hydrocarbons (C. J. 37, 702). Substitution may take place either in the nucleus or in the methyl group of toluene. In the former case a mixture of para- and ortho- compounds is chiefly formed.

Toluene is employed in the manufacture of nitrotoluene and toluidine, benzyl chloride, benzal chloride, and benzotrichloride, benzaldehyde, benzoic acid, and cinnamic acid. Formerly toluene formed an essential ingredient of the benzene employed as the starting-point in the manufacture of magenta, but at the present day it is usual to start with pure benzene and pure toluene.

Commercial toluene should give only a pale-brown colouration with concentrated sulphuric acid. On distillation a crude toluene should distil to at least 90 p.c. under 120°; and the 'pure toluene' of commerce should distil between 110–113°—the greater part between 111–112° (Schultz, Chem. des Steinkohlentheers).

Unless coal-tar toluene has been purified by shaking it with concentrated sulphuric acid, it always contains α- and β- thiotolen (methylthiophen).

Chlorine Derivatives of Toluene.

In the chlorination of toluene, substitution may, as already mentioned, take place either in the nucleus or in the methyl group. The former is the case when chlorine acts on toluene in presence of iodine or other substances capable of acting as carriers of chlorine; the latter, when chlorine alone acts on toluene heated to boiling or exposed to direct sunlight, the influence of light being greater than that of heat in inducing substitution in the side-chain (Schramm, B. 18, 608). Only the chlorine derivatives belonging to the latter class are of technical importance.

Benzyl chloride $C_6H_5.CH_2Cl$. First obtained by Cannizzaro by the action of hydrochloric acid on benzyl alcohol $C_6H_5.CH_2.OH$. Manufactured by passing chlorine into boiling toluene contained in large glass flasks and exposed to sunlight. The operation is interrupted when the toluene shows the theoretical increase of weight (37·5 p.c.). The vapours are condensed by a reflux worm, and the escaping hydrochloric acid passed into water. The product is shaken with weak alkali and then rectified, by which means it is freed from unaltered toluene and higher chlorinated products.

Colourless liquid; boiling at 176°; sp.gr. at 14°, 1·107. Has a somewhat pungent smell; the vapour is very irritating to the eyes. Insoluble in water, but by heating with water to 100–110°, or by boiling with water for 24 hours with a reflux condenser, it is converted into benzyl alcohol (Niederist, A. 196, 353); and the same transformation is still more readily effected by boiling benzyl chloride with the calculated quantity of potassium carbonate dissolved in from 8 to 10 parts of water (Meunier, Bl. 38, 159). Oxidising agents convert it first into benzaldehyde, afterwards into benzoic acid. By heating with a small quantity of copper it yields dibenzyl $C_6H_5.CH_2.CH_2.C_6H_5$. With alcoholic ammonia it gives a mixture of benzylamine $C_6H_5.CH_2.NH_2$, dibenzylamine $(C_6H_5.CH_2)_2NH$, and tribenzylamine $(C_6H_5.CH_2)_3N$ (Cannizzaro, A. 134, 128; A. Suppl. 4, 24, 80). With aniline it forms benzylaniline

$$C_6H_5.CH_2.NH.C_6H_5.$$

Benzyl chloride is used in the preparation of benzaldehyde and benzoic acid, and also for introducing the benzyl group into basic colouring matters so as to produce varieties of shade.

Commercial benzyl chloride generally contains moisture, benzal chloride ($C_6H_5.CHCl_2$), benzotrichloride ($C_6H_5.CCl_3$), chlortoluenes, and even unchanged toluene. It should show the correct boiling-point and specific gravity. In order to ascertain whether the whole of the chlorine is contained in the methyl group, K. E. Schulze (B. 17, 1675) recommends that a weighed quantity of the substance should be boiled for some minutes with a hot saturated alcoholic solution of silver nitrate, using a reflux condenser; the silver chloride, which will represent only the chlorine from the side-chain, is then collected and weighed. Benzotrichloride may be detected by the green colouring-matter (malachite green) which is formed when the substance is heated with dimethylaniline and zinc chloride (Döbner).

Benzal chloride. *Benzylidene chloride*
$C_6H_5.CHCl_2$.
First obtained by Cahours (A. Ch. [3] 23, 329) by the action of phosphorus pentachloride on benzaldehyde $C_6H_5.CHO$. Manufactured by chlorinating boiling toluene in direct sunlight.

Colourless, powerfully refractive liquid, boiling at 206°; sp.gr. 1·2557 at 14°. Water, alkalis, or concentrated sulphuric acid, convert it into benzaldehyde. When heated with sodium acetate it yields cinnamic acid.

Benzal chloride is employed in the manufacture of benzaldehyde, benzoic acid, and cinnamic acid.

The commercial product is always impure. It may be tested by its boiling-point, and by determining the percentage of chlorine.

Benzotrichloride. *Phenylchloroform*
$C_6H_5.CCl_3$.
First obtained by Schischkoff and Rösing (C. R. 46, 367) by the action of phosphorus pentachloride on benzoyl chloride $C_6H_5.COCl$. Manufactured by chlorinating boiling toluene in direct sunlight until the weight of the product no longer increases.

Colourless, powerfully refractive liquid, boiling at 213–214°; sp.gr. 1·380 at 14°. Heated with water at 150°, it yields benzoic and hydrochloric acids. Sodium ethoxide converts it into ethyl orthobenzoate $C_6H_5.C(OC_2H_5)_3$. Heated with dimethylaniline and zinc chloride, it yields malachite green. Methyldiphenylamine, diethylaniline, and diamylaniline give similar green colouring matters, differing in shade from malachite green.

Benzotrichloride was formerly employed in the manufacture of malachite green, but owing to the difficulty of obtaining benzotrichloride in a state of purity this process has been abandoned.

Commercial benzotrichloride is tested by examining its boiling-point. It generally contains compounds chlorinated in the nucleus.

F. R. J.

TOLUIDAZINE *v.* Azines.

TOLUNAPHTHAZINES *v.* Azines.

TOLUPHENAZINE *v.* Azines.

TOLUQUINOL. *Tolu hydroquinone v.* Phenol and its homologues.

TOLUSAFFRANINES *v.* Azines.

TOLUYLENE-DIAMINES. *Diamido-toluenes v.* Diamines.

TOLUYLENE BLUE *v.* Indamines and Indophenols.

TOLUYLENE ORANGE. Toluylene orange is the name of a mixed tetrazo- dye produced by combining cresolcarboxylic acid and toluylenediamine sulphonic acid with tetrazoditolyl. It is sold in two shades, G (TO G) and R (TO R).

The commercial product is the sodium salt. It appears as an orange-brown powder, tolerably easily soluble in water. Its aqueous solution is rendered brighter in colour by the addition of a little caustic soda; further addition produces an orange-brown precipitate. Concentrated sulphuric acid dissolves the dye with a violet colour.

Toluylene orange G (TO G) was the first orange substantive dye which appeared in the market. It yields shades fast to soap, and ranging from the most delicate 'ivories' and 'creams,' through the whole scale of buffs, down to full shades of orange closely resembling chrome orange, but possessing advantages over the latter in not being tarnished by hydrogen sulphide and not injuring the feel of the cloth. Again, the shades are faster to acids than chrome orange, and faster to light than the reds of the substantive class. The dye is very suitable in calico printing for the production of pad buffs and creams, and is strongly recommended as a substitute for iron buff, especially for padding over colours liable to be injured by this colour. Chrysamine, which has been in use some time as a substitute for iron buff, is not as red as the latter, and no satisfactory method of overcoming this deficiency is known. The various methods in use, such as leaving the pink stain uncleared on cloth printed with alizarin colours, mixing caustic soda with the chrysamine, and adding magenta or benzopurpurin to the padding colour, all have their drawbacks. Toluylene orange, again, is not so sensitive as chrysamine to the action of copper salts or metallic copper. It is best applied in a wooden dye-bath along with soap and phosphate of soda, the water being first softened by boiling with soap and the scum removed. In dyeing full shades on cloth printed with fast colours the bath may be boiled; in the case of cloth printed with aniline colours, the temperature should not exceed 45°. Eight to ten minutes dyeing will suffice for printed cloth; plain cloth should be worked at the boil for a longer time. In the case of medium and pale shades, it is preferable to pad either by padding or printing machine, since the dye is apt to be too rapidly, and consequently unevenly, absorbed from a dye-bath. The following receipt is given for a medium pad shade: 2 parts of toluylene orange G are dissolved in 1,000 parts of boiling water containing 20 parts of sodium phosphate and 5 parts of soap. The solution is then mixed with 1,000 parts of gumt ragacanth paste (1 : 20) and boiled for fifteen minutes, then strained and padded. The pieces are passed through a Mather & Platt's steam aniline ager, or steamed for a short time, washed, and finished.

The steaming can be dispensed with in many cases, and the pieces finished after lying for a few hours.

A printing colour is made by mixing starch paste, gum tragacanth paste, toluylene orange G, and glycerin. The calico is printed, steamed for an hour, and washed in a cold bath containing 3 per cent. of ground chalk. The colour is not very fast to soap, but is suitable for many purposes—such as linings, for example.

Discharge effects are obtained by printing a thickened mixture of stannous acetate for white, and Persian berries, alizarin, methylene blue, alizarin blue, logwood, along with suitable mordants, and stannous acetate for coloured patterns.

Toluylene orange acts as mordant for basic dyes, and a variety of compound shades can thus be obtained. Care must be taken that the material dyed with the orange is well rinsed before the basic dye is applied.

Linen and jute dye similarly to cotton; China grass and hemp take a redder shade. Animal fibres dye under the same conditions as the vegetable fibres, and are coloured more yellow than the latter. Silk dyes well in baths of boiled-off liquor 'broken' with acid. Wool is dyed for an hour at the boil in a bath containing 10 p.c. of sodium sulphate; the shades obtained are fast to milling.

Toluylene orange R in general resembles the G shades, but gives redder shades, which are, however, scarcely so fast. Salmon shades are obtained by using only a little of the dye; larger quantities give shades like chrome-orange which has been strongly limed or topped with magenta. Toluylene orange R is applied in the same way as the G shade (F. V. Kallab, Mittheil. des k. k. Tech. Gew. Museums, 1888, 114–120; S. C. I. 8, 540).

TOLUYLENE RED *v.* Azines.

TONITE *v.* Explosives.

TONKA BEAN. *Tonquin bean* (*Fève tonka*, Fr.; *Tonkabohnen*, Ger.). The seed of the fruit of the leguminous tree *Dipterix odorata* (Willd.) which inhabits Guiana and Venezuela. Each pod contains a single seed, which is about two inches long and half an inch wide. It has a dark-brown colour, is deeply wrinkled externally, and characterised by an agreeable odour and bitter aromatic taste. The tree flourishes in the forests of the Caracas district of Venezuela The first crop of beans is gathered when the tree is three years old, but a full crop is not obtained until two years later. The fruit bears some resemblance to a small mango, and contains the odorous bean in its centre. According to the report of Consul Mansfield, the exports from Venezuela alone in 1883 were five thousand quintals (Ph. [3] 14, 749). The seed of *D. oppositifolia*, the so-called English Tonka bean, has similar properties to that of *D. odorata*, but it is smaller and darker in colour.

Besides sugar, gum, malic acid, and woody fibre, tonka bean contains *fixed oil* and about 1·5 p.c. of *coumarin* (Boullay a. Boutron-Charlard, J. Ph. 11, 480). It is to the presence of coumarin that the odour and taste of the seed is due, and crystals of this compound often occur as an efflorescence on commercial specimens. To extract the coumarin, the finely-chopped beans, according to Gössmann, are heated for some time nearly to boiling with an equal bulk of 80 p.c. alcohol; the whole is then filtered and the residue again heated in the same manner; the extracts are mixed together, and the alcohol removed by distillation till the residue becomes turbid, when it is mixed with four times its volume of water, which precipitates the coumarin in somewhat impure crystals. Adhering fat may be removed by heating the mixture to boiling, and filtering through a moistened filter. On cooling, the crystals which re-dissolve in the hot liquid again separate, and they may be further purified, if necessary, by treatment with animal charcoal (A. 98, 66; Gm. 13, 322), *v.* Coumarin.

Tonka bean is largely used to flavour tobacco, and especially snuff, as an ingredient of sachet powder, and in alcoholic solution as a flavouring essence. A. S.

TOPAZ, ORIENTAL, *v.* Corundum.

TOPAZ, SCOTCH, *v.* Cairngorm.

TOPAZ, SPANISH, *v.* Cairngorm.

TORBANITE or **TORBANEHILL MINERAL** *v.* Paraffin.

TORMENTILLA. The roots of *Tormentilla erecta* have been occasionally substituted for those of rhatany in medicine. They contain from 5 to 6 p.c. of a tannin, giving a dark-green precipitate with ferrous sulphate, bluish-red with ferric acetate; is also precipitated by gelatin and by tartar-emetic (Stenhouse).

TORREFACTION. Roasting ores in order to expel volatile substances, *e.g.* sulphur, arsenic, &c.

TOULOUCOUNA or **TULUCANA OIL.** An oil obtained by pressing the kernels of *Carapa guianensis v.* Carapa bark.

TOULOURON OIL. A brown oil obtained from *Pagarus Latro.* Used in Senegal as a remedy for rheumatism.

TOURMALINE. A mineral silicate, of complex and variable chemical composition. Rammelsberg has classified the numerous varieties under the heads of magnesia tourmaline, iron-magnesia tourmaline, iron tourmaline, iron-manganese-lithia tourmaline, and lithia tourmaline. For discussion of its composition, *v.* Rammelsberg, in P. 139, 379, 547. P. Jannasch and G. Calb have published nine analyses (B. 22, 216), whence they deduce the general formula $R_9BO_2(SiO_4)_2$. A green tourmaline from Brazil yielded them: SiO_2, 37·05 p.c.; B_2O_3, 9·09; F, 1·15; Al_2O_3, 40·03; FeO, 2·36; MnO, 2·35; CuO, 0·47; MgO, 0·32; Li_2O, 0·60; K_2O, trace; Na_2O, 3·18; H_2O, 3·23.

Tourmaline crystallises in the rhombohedral system, usually in the form of prisms with longitudinal striations. In transverse section the prisms are triangular, hexagonal, or polygonal, the number of sides being multiples of three. The prisms are usually terminated by rhombohedral faces, but in many cases the two ends are dissimilar, and then, as is common with hemimorphic crystals, they exhibit electric polarity when heated.

The colours of tourmaline are very variable, and have given rise to numerous varietal names. Colourless tourmaline is rare, but some of the crystals in the granite of San Pietro, in Elba, are practically colourless, and are hence known as *achroite.* The finest coloured tourmaline is the red, usually termed *rubellite*, while from its occurrence in Siberia it is sometimes known as 'Siberian ruby.' Upper Burma also yields fine rubellite, and the workings, now mostly deserted, have been visited by Mr. Barrington Brown and by Dr. Noetling. The mineral occurs as rolled pebbles in gravel and conglomerate, probably derived from gneissose rocks. In China the rubellite is highly valued for buttons on the caps of mandarins of high rank. Blue and green tourmalines are obtained from Brazil, the blue being known as *indicolite* and the green sometimes as 'Brazilian emerald.' The mineral is also brought, for the purposes of the jeweller, from Ceylon; and the word tourmaline is, in fact, said to be derived from the Cingalese. The colours of the mineral are generally too dull to be much appreciated, except by connoisseurs; but some of the American crystals are very brilliant, especially those from Paris and Hebron in Maine, and from Chesterfield, in Massachusetts. Some of these crystals exhibit a red nucleus surrounded by a zone of green, whilst other prisms are red at one end and green at the other. Parti-coloured crystals are also not uncommon in Elba.

Transparent crystals of tourmaline are valued for their optical properties, the green and brown varieties being most used. The mineral is strongly dichroic. A thin plate cut parallel to the vertical axis of a crystal will absorb the ordinary ray and transmit only the extraordinary ray; hence it can be used as either polariser or analyser. Two plates, secured in cork and mounted in rotating rings attached to a spring-wire holder, form the instrument known as the 'tourmaline tongs,' much used by spectacle-makers for distinguishing rock-crystal, or 'pebble,' from glass.

Tourmaline is only slightly harder than quartz ($H = 7·5$), but is much denser (sp.gr. 2·94 to 3·3).

Black tourmaline is generally known under the name of *schorl*, which is said to be an old German mining term. Fine black crystals are brought from Madagascar, and splendid crystals were found many years ago near Bovey Tracey, in Devonshire. Schorl is a common mineral in granite and gneiss, especially in the neighbourhood of tin-lodes. It is generally found near the margin of an intruded mass of granite, and appears to be a secondary product due to the action of vapours carrying boric and hydrofluoric acids. *Schorl rock* is an aggregate of black tourmaline and quartz, and may perhaps be regarded as an altered granite. The beautiful but rare Cornish rock *Luxullianite* contains much tourmaline, associated with quartz and felspar. Small crystals and rolled grains of tourmaline are common in sands derived from the disintegration of crystalline rocks.

F. W. R.

TOUS-LES-MOIS is a species of arrowroot procured from the tubers of *Canna edulis*, nat. ord. *Marantaceæ.* The starch is obtained in the same manner as other descriptions of arrowroot. Under the microscope the granules show themselves to be unusually large, measuring from ·0015 to ·0037 inch in length and from ·001 to to ·0027 in breadth; broad, flat, ovate. The hilum is situated at the narrow extremity, and the rings are very close, firm, and regular.

Tous-les-mois is used for mixture with cocoa preparations and as a food for infants, for which latter purpose it is bleached.

TOWN TALLOW *v.* Tallow.

TRAGACANTH. *Tragacanthin v.* Gums.

TRAVERTINE. A limestone deposited by calcareous springs, known also as *calc sinter* and *calcareous tufa.* The typical travertine occurs near Tivoli, the ancient Tibur, whence the name *lapis Tiburtinus* applied to it by Vitruvius and Pliny. The most important sources at this locality are the sulphuro- calcareous springs, known as the Acque Albule, surrounded by a plain representing the floor of an ancient lake, and consisting of thick beds of travertine. This stone, being easily worked and of great durability, and presenting a pleasing tone, has for ages been the favourite building material in Rome. The quarries of Barco, on the Aniene, furnished the stone for the Coliseum, and those of Fosse the material for St. Peter's. To supply modern Rome new quarries have been opened at the Villa Adriana, below Tivoli (N. Pelati, 'I Travertini della Campagna Romana,' Rome, 1882; P. Zezi, in Johnston-Lavis's 'South Italian Volcanoes,' Naples, 1891).

Springs issuing from limestone rocks commonly precipitate calcium carbonate upon objects with which they come in contact, and are thus improperly termed 'petrifying springs.' Calcareous incrustations are formed, for instance, by water issuing from the carboniferous limestone at Matlock, in Derbyshire; whilst extensive accumulations of tufa are produced by the thermal springs of Clermont, in Auvergne, and of Hieropolis, in Asia Minor. Some of the freshwater limestones of the oligocene series of the Isle of Wight were probably formed as tufaceous deposits in lakes.

The deposition of travertine, or tufa, may result from the mere exposure of highly calcareous waters to atmospheric influences, carbonic acid being removed and the normal calcium carbonate precipitated. Agitation of the water facilitates the loss of carbonic acid, and hence calcareous deposits often occur where the water falls in a spray or cascade. Deposition is also favoured by the action of heat, by diminution of pressure, and by the agency of plants. It was shown by F. Cohn that in the hot springs of Karlsbad microscopic plants are important agents in determining the deposition of calcareous tufa, or *Sprudelstein.* At the Mammoth Hot Springs in the Yellowstone National Park algæ are always present, though the temperature may be as high as 73°C., and it is believed that such plants are important factors in the formation of the travertine at this locality (*v.* W. H. Weed, in 9th Annual Rep. U. S. Geol. Survey, Washington, 1889). F. W. R.

TREACLE *v.* Sugar.

TREE WAX *v.* Wax.

TRENT SAND. A sand found in the Trent, Severn, and in other rivers; used for polishing.

TRIDECATOIC ACID or **TRIDECYLIC ACID** *v.* Fatty acids.

TRIGONELLINE *v.* Vegeto-alkaloids.

TRIMETHYLACETIC ACID *v.* Fatty acids.

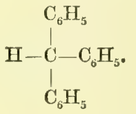
TRIMETHYLBENZENES *v.* Cumenes.

TRINITROPHENOL *v.* Picric acid.

TRIPHENYLMETHANE COLOURING MATTERS. This is the generic name of a very large and varied class of artificial dye-stuffs, which have been obtained by very different methods. Some of the oldest artificial dye-stuffs belong to this group. Their generic connection was, in many instances, not known until their constitution was fully cleared up. When this had been done, a large number of new dye-stuffs belonging to the same class was prepared by direct synthesis. The members of this group vary more than those of any other in their physical properties; they represent almoste very possible shade, and include dye-stuffs suitable for every kind of dyeing and printing process. They are applicable to silk, wool, and cotton dyeing; as a rule, they are of very pure and brilliant shades—in fact, the most brilliant of all colouring matters are found amongst them. Many are rather fugitive, especially the older ones—magenta-red and its congeners. It is for this reason that aniline dyes generally have been declared fugitive and unstable by people of hasty judgment. This want of stability is, however, not characteristic of the members of the triphenylmethane group; some of the best and most permanent dye-stuffs belong to it. It may be well to remark at once, that resistance to light and other influences seems not to be directly related to the chemical constitution of these substances, as it is frequently observed that of two dye-stuffs of very similar constitution one may be very fugitive, whilst the other is remarkable for its fastness.

The members of this family are not, like those of the azo- group, connected by one generic method, by which all of them might be produced from various materials. Nor is it possible to enumerate a number of general synthetic methods which result in their production. The methods applicable are so numerous that no generalisation is possible. The only connecting link between all these dyes is their chemical constitution, which is now well established in almost every case; it is also in this constitution that we find the necessary criteria for the subdivision of the group. Some introductory remarks about the constitution of these dyes are therefore necessary for a complete revision of the subject.

If we consider the constitution of these colouring matters, we observe that there is but one characteristic feature common to them all. This is the presence of an atom of carbon connected by three of its atomicities to three aromatic radicles. The compound of the simplest constitutional formula in which this 'central carbon' (as we will henceforth call it) is observed is the hydrocarbon triphenylmethane, the formula of which is $C_{19}H_{16}$:

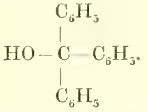


$$\begin{array}{ccc} & C_6H_5 & \\ & | & \\ H- & C & -C_6H_5. \\ & | & \\ & C_6H_5 & \end{array}$$

Triphenylmethane thus becomes the prototype of all the members of this group; it is for this reason that the name of *triphenylmethane colouring matters* was chosen.

Triphenylmethane was first prepared by Kekulé and Franchimont, in 1872, by heating benzylidene chloride with mercury diphenide to 150° (B. 5, 907). Its formation has since been observed in numerous reactions. The best method for preparing it consists in treating a mixture of two parts of chloroform and seven parts of benzene with aluminic chloride, until no more hydrogen chloride is given off. The resulting liquid is washed with water and dried. On distillation it yields benzene, di-phenyl-methane, and tri-phenyl-methane. The latter may be purified by crystallisation. This method was indicated by Friedel and Crafts (A. Ch. [6] 1, 489). Triphenylmethane is obtained in colourless crystals; m.p. 92°; b.p. 358–359°. It is capable of forming a molecular combination with benzene. Of its derivatives the following two are important on account of their relations to the colouring matters under consideration.

Triphenyl carbinol $C_{19}H_{16}O$ is the tertiary alcohol derived from triphenylmethane:



$$\begin{array}{c} C_6H_5 \\ | \\ HO-C-C_6H_5. \\ | \\ C_6H_5 \end{array}$$

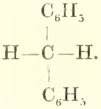
It is easily obtained by oxidising the hydrocarbon by means of chromic acid. It forms colourless crystals, melting at 159° and distilling at 360° (E. and O. Fischer, A. 194, 271).

Trinitro-triphenylmethane $C_{19}H_{13}N_3O_6$ is obtained by treating the hydrocarbon with strong nitric acid. Crystals, melting at 203°. Chromic acid transforms them into trinitro-triphenylcarbinol (E. and O. Fischer, A. 194, 256).

Neither of the above substances is a colouring matter, nor are they even coloured. But if we reduce trinitro-triphenylcarbinol by adding zinc-dust to its solution in acetic acid, we obtain triamidotriphenylcarbinol, which is identical with pararosanilin. By showing this identity, E. and O. Fischer solved the problem of the constitution of this very important colouring matter. Leucaniline, the reduction product of rosaniline, was shown to be identical with triamidotriphenylmethane. This discovery became the starting-point for very important theoretical and practical work. All the congeners of rosaniline were shown to be derivatives of triphenylmethane or analogous hydrocarbons, and new synthetical methods were devised by which such derivatives could be obtained.

It is quite obvious that not only triphenylmethane, but also all its homologues and analogous hydrocarbons, are parent substances of dye-stuffs. The number of such hydrocarbons indicated by the theory of the aromatic series is very large, since every one of the three phenyl radicles connected with the central carbon may be replaced by any other aromatic radicle. Every one of the hydrocarbons thus formed is capable of yielding, like triphenylmethane itself, a very large number of colouring matters, as will be seen from subsequent considerations. It thus becomes evident that the theoretical number of possible triphenylmethane colouring matters is almost unlimited. It has, however, been shown that the variation of the aromatic radicles connected with the central carbon is but of small importance for the variation of the shades and properties of the resulting dye-stuffs. The triphenylmethane colouring matters in actual use are the derivatives of a very few hydrocarbons, of which triphenylmethane itself is by far the most important. Tolyldiphenylmethane, ditolylphenylmethane, tritolylmethane, and naphthyldiphenylmethane are the exclusive parent substances of about seventy-five colouring matters, which at present form the object of regular and extensive manufacture, and of several hundred more which have been prepared and patented without coming into general use. The extensive range of shade and general applicability, so characteristic of the colouring matters of this class, and unequalled by any other class of dye-stuffs known, is not so much a result of the variation of the hydrocarbons forming their parent substances, as of the extremely large number of coloured derivatives which may be produced from every one of these hydrocarbons. No other branch of the chemistry of dye-stuffs is so extremely fertile in the synthetical methods at its disposal as this, and every one of these methods forms an easy way for the production of a considerable number of dye-stuffs, which can generally be produced by this one method alone, or by but a few others. Many of these methods, both empirical and synthetical, have been patented, and some of these patents are of great value and importance. They are generally good patents, claiming new processes; in this respect they form the exact counterpart of the still more numerous patents for azo- colouring matters, which, being all based on the same method of work, only claim the novelty of the product obtained by varying the ingredients of the process.

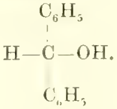
Before entering into the details of the constitution of triphenylmethane dye-stuffs, and the connection of this constitution with the properties of the dyes, we have to describe another substance closely related to triphenylmethane, some of the derivatives of which are dye-stuffs similar to those derived from triphenylmethane itself, whilst others play an important part in the processes for the production of triphenylmethane colouring matters. This substance is also a hydrocarbon, derived from methane by replacing only two of its hydrogen atoms by the aromatic radicle phenyl. This hydrocarbon is *Diphenylmethane*, or benzyl-benzene $C_{13}H_{12}$:



$$\begin{array}{c} C_6H_5 \\ | \\ H-C-H. \\ | \\ C_6H_5 \end{array}$$

It was discovered by Zincke in 1873 (A. 159, 374), and is best prepared by the method indicated by Friedel and Balsohn (Bl. 33, 337), by adding aluminic chloride to a mixture of 1 part benzylic chloride with 5 parts of benzene. It melts at 26–27°C., and boils at 261–262°. It forms white crystals, possessing an agreeable odour of oranges. Of its derivatives the following are of practical importance:—

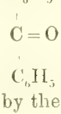
Diphenylcarbinol or **benzhydrol** $C_{13}H_{12}O$ is the corresponding alcohol:



$$\begin{array}{c} C_6H_5 \\ | \\ H-C-OH. \\ | \\ C_6H_5 \end{array}$$

It is prepared by boiling benzophenone with alcoholic potash solution and zinc-dust. It forms white crystals, melting at 67·5–68°, boiling at 297–298° (Linnemann, A. 133, 6; Zagoumenny, A. 184, 174).

Benzophenone $C_{13}H_{10}O$ is the second product of oxidation of diphenylmethane, to which it stands in the same relation as that which exists between propane and acetone. Benzophenone is the typical ketone of the aromatic series:



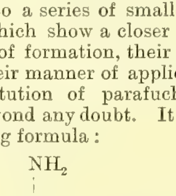
$$\begin{array}{c} C_6H_5 \\ | \\ C=O. \\ | \\ C_6H_5 \end{array}$$

It is best prepared by the process which led to its original discovery, by distilling calcic benzoate, or, better still, by distilling a mixture of calcic and zincic benzoate. Another process consists in adding aluminic chloride to a solution of carbonyl chloride $COCl_2$ (phosgene) in pure benzene, or to a mixture of benzene with benzoylic chloride. Benzophenone forms beautiful prismatic crystals, melting at 48–48·5°, distilling at 305°C. (Péligot, A. 12, 41; Chancel, A. 72, 279; Friedel, Crafts a. Ador, B. 10, 1854).

The amido- derivatives of diphenylmethane, diphenylcarbinol, and benzophenone, which are of special importance for the chemistry of the triphenylmethane dye-stuffs, will be described later on in connection with the dye-stuffs to which they give rise.

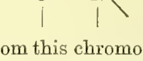
The substances mentioned so far, although the parent substances of so many beautiful and powerful dyes, are all perfectly colourless. Even triamidotriphenylcarbinol, which is identical with pararosaniline, is perfectly colourless; it only becomes a dye-stuff by being dissolved in an acid, a reaction from which one might infer that parafuchsine, the typical magenta colour, is merely a salt of pararosaniline. This is, however, not the case, although colour-makers are apt to call, for simplicity's sake, the rosanilines 'magenta bases.' The dissolution of any or either of the amidated carbinols is invariably accompanied by a condensation in the molecule, and a loss of one molecule of water. The basic triphenylmethane colouring matters are therefore free from oxygen (unless they contain it in the shape of water of crystallisation); if we decompose the salts, by the addition of an alkali, coloured bases are formed, which, however, are very unstable. They take up, at once, one molecule of water, and re-form the original colourless or faintly-coloured carbinol base. By this observation it is clearly shown that something more than the presence of the 'central carbon' is necessary for the formation of a triphenylmethane colouring matter. We have, therefore, to consider the constitution of the colouring matters themselves to obtain a knowledge of the chromophoric group of these dye-stuffs. This consideration leads at the same time to an easy and useful classification, to a subdivision into a series of smaller groups, the members of which show a closer connection in their methods of formation, their physical properties, and their manner of application.

The constitution of parafuchsine is now established beyond any doubt. It is represented by the following formula:



This formula shows also the typical constitution of all the congeners of magenta, every one of which may be represented by a similar formula, in which either one or more of the phenyl radicles are replaced by other aromatic radicles, or one of the amido- groups replaced by hydrogen, or one of the six available hydrogen atoms of the amido- groups replaced by radicles of the fatty or aromatic series, or several of these changes introduced at the same time. It will at once be obvious that several thousand different combinations may thus be produced, all colouring matters of different shades, but showing in their properties a general resemblance to parafuchsine. The constitutional formulæ of all these colouring matters have but one thing in common besides the 'central carbon' (which is, as has been said, characteristic not only of these, but also of all the other triphenylmethane colouring matters); this one essential feature is the connection between the central carbon atom and the pentavalent nitrogen. We have, therefore, a perfect right to claim this invariably present carbon-nitrogen group as the essential group of the whole molecule, and as the cause of its being a colouring matter. This group we may, therefore, call the chromophoric group of the fuchsine family.

If we remove this group from its connection with all variable constituents of the molecule, we obtain it in this shape:



If, starting from this chromophoric group, we attempt to give a general formula for the fuchsine family, we may do so by introducing the letters

R^{II} for a bi-valent radicle of the aromatic series.

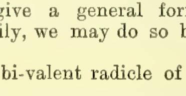
R^{I} for a monovalent radicle of the aromatic or fatty series replaceable by hydrogen.

X for a salt-forming group of any kind, replaceable by hydrogen.

S for an acid radicle of any kind replaceable by hydroxyl.

We thus obtain the typical formula:

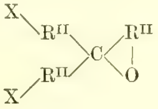
1.



It is this formula which we shall use as a basis in giving the constitution of the various members of the fuchsine group, to be enumerated later on.

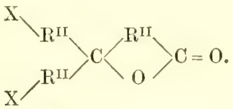
Before, however, proceeding to this enumeration, we will consider the changes which may be brought about in this formula without disturbing its typical character by replacing the general signs (R^{I}, R^{II}, X, S) by actual chemical radicles. It will at once be seen that there is only one possibility for such a change. The central carbon cannot be removed; we have no other tetravalent atom at our disposal, excepting silicium, which, so far, plays no part in the methods of organic synthesis. Besides this, we would, by removing the central carbon, disturb the triphenyl methane arrangement. If, therefore, we wish to change anything, we can only do so by replacing the pentavalent nitrogen atom by another suitable group. But this group need not necessarily be pentavalent. Of the five nitrogen valencies only two are absolutely necessary for forming the typical arrangement, viz. the one forming connection with the central carbon, and the one forming connection with one of the R^{II} radicles. We may, therefore, replace the pentavalent nitrogen by a bivalent atom or group. Of such groups only two have proved of value for the production of dye-stuffs. These two are O^{II} oxygen, and the bivalent group —O—CO—. We thus obtain two new families or groups of triphenylmethane colouring matters, which may, like the fuchsine group, be represented by typical general formulæ, in which the same general signs may be used. These groups of dye-stuffs are—

2. The aurine group:



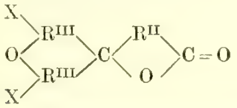
and

3. The phthaleine group:



For this latter group a new feature is introduced, and at the same time the number of available dye-stuffs is limited by the fact that only those of its members are useful dye-stuffs in which the two R^{II} radicles on the left side of the central carbon are linked together by a bivalent group, which consists almost invariably of an oxygen atom. We may, therefore, at once modify the typical formula by introducing this oxygen link after changing the two radicles R^{II} into R^{III}, by introducing another valency, to which the oxygen atom may be attached:

4.



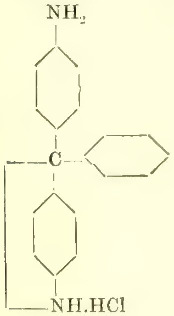
Typical formula of phthaleine dye-stuffs in actual use.

We now proceed to give a detailed account of these three groups and their various members.

I. The Fuchsine Group.

(A) *Diamidotriphenylmethane derivatives.* The simplest type of these colouring matters is

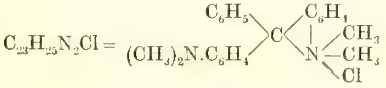
1. **Benzaldehyde violet** $C_{19}H_{17}N_2Cl =$



which may be prepared from diamidotriphenylmethane by oxidation. The yields are, however, very poor, and the colour itself is of no great value. Its manufacture has, therefore, never been attempted.

The derivatives of this substance, however, in which the hydrogen of its two amido- groups is replaced by various radicles of either the fatty or aromatic series, are of great value and importance. Of these, the oldest, best known, and simplest in its constitution, is

2. **Benzaldehyde green.** (Syn. *Malachite green, New green, Victoria green, Fast green, Diamond green, Benzoyl green, Benzal green.*)



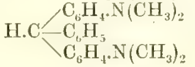
$$C_{23}H_{25}N_2Cl = \begin{matrix} C_6H_5 \\ (CH_3)_2N.C_6H_4 \end{matrix} > C < \begin{matrix} C_6H_4 \\ | \\ N \begin{matrix} -CH_3 \\ -CH_3 \\ -Cl \end{matrix} \end{matrix}$$

This product was discovered almost simultaneously by Otto Fischer (1877; B. 10, 1625) and O. Döbner (1878; B. 11, 1236), who prepared it by different methods. For some time it was believed that Döbner's product was different from Fischer's until their identity was finally established. Döbner's process was patented (Germ. Pat. No. 4,322). Fischer's process proved, however, more practical, and has since been generally adopted.

Fischer's process gave bad yields and a poor product at first, until the best method for its manufacture was discovered. It consists in the following operations:—

(*a*) Manufacture of tetramethyldiamidotriphenylmethane by the reaction of benzoic aldehyde on dimethylaniline:

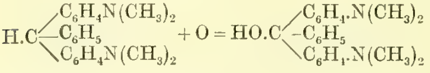
$$C_6H_5.COH + 2C_6H_5N(CH_3)_2 = H_2O +$$



$$H.C \begin{matrix} \diagup C_6H_4.N(CH_3)_2 \\ -C_6H_5 \\ \diagdown C_6H_4.N(CH_3)_2 \end{matrix}$$

The base obtained in this reaction is generally called 'green leuco- base' by the manufacturers. For preparing it one molecule of benzoic aldehyde is mixed with very little more than two molecules of an absolutely pure dimethylaniline, and a substance capable of absorbing the water formed in the reaction is added. Dry zinc chloride was originally prescribed, and is still used by many manufacturers. Its quantity should be equal in weight to the aldehyde employed. Hydrochloric, sulphuric, or oxalic acid, or sodic bisulphate may be used instead of the zinc salt. The mixture is heated in a jacketed still to 100–110°C. for about forty-five to forty-eight hours. The product is then transferred into a still, a sufficient quantity of caustic soda is added to make the mixture alkaline to test-paper, and a current of steam is blown through the liquid in order to remove every trace of dimethylaniline and benzoic aldehyde. The leuco- base is not volatile; it remains in the still in the shape of a viscid mass, which solidifies into white crystals after a while. This base is now subjected to the second operation.

(*b*) Oxidation into green. It is here that great difficulties were encountered in the beginning of the manufacture. Special conditions are required to obtain a good crystallisable dye-stuff. If these are not strictly adhered to, a non-crystallisable green is the result. The latter is probably different from the crystallisable substance in composition, containing one methyl group less, which is lost in the shape of formic aldehyde by a too powerful action of the oxidising agents. The following conditions give excellent results: 33 kilos of leuco- base are dissolved in 25 kilos of ordinary hydrochloric acid, and diluted with 200 litres of water; 30 kilos of ordinary acetic acid of 45–50 p.c. are then added. It is necessary that these two acids should be present; neither of them can be replaced by another acid of equal strength. The solution is then oxidised in the cold (in the summer it is advisable to add some ice) with a paste of plumbic peroxide of known strength. The peroxide should be tested by the oxalic acid method (determination of the CO_2 evolved from an excess of oxalic acid by the peroxide in question), and not by the iodometric method, as the latter gives too high results. Every sample of plumbic peroxide contains a certain amount of crystalline peroxide, which does not act on the leuco- base. This does not act on oxalic acid either, whilst the iodometric method gives values for both modifications indiscriminately. For oxidising the leuco- base the exact quantity of peroxide should be taken, which is indicated by the following equation:



$$H.C\begin{cases}C_6H_4N(CH_3)_2\\C_6H_5\\C_6H_4N(CH_3)_2\end{cases} + O = HO.C\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_5\\C_6H_4.N(CH_3)_2\end{cases}$$

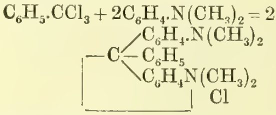
One molecule of peroxide is, therefore, required to every molecule of the base.

As soon as the peroxide has been added, under constant stirring, the liquid turns a deep green. From this liquid the dye-stuff may be separated by different methods; an addition of zinc chloride solution is generally recommended. This, however, precipitates both the crystalline green and the tarry modification which is never quite absent. The following process has given excellent results in the hands of the writer.

The green liquid obtained by oxidation is saturated with common salt and left to itself. Very soon small glittering scales of the lead double chloride of the crystallisable green make their appearance.

They are collected on a filter. From the mother-liquor an inferior quality of green may be obtained by adding a solution of sodic sulphate, filtering, and precipitating with zinc chloride and common salt. The crystals of the lead double chloride are dissolved in hot water. Sufficient sodic sulphate is added to precipitate the lead. The liquid is then filtered and precipitated with ammonia. The 'green base' (tetramethyl-diamidotriphenyl carbinol) settles out in the shape of a pink precipitate, which is filtered off and washed. From it the 'green crystals' of commerce may be prepared, either by dissolving it in a hot solution of oxalic acid and allowing the liquid to cool very slowly, or by dissolving it in dilute hydrochloric acid and adding a solution of zinc chloride. Besides these two the iron double salt is also occasionally met with in commerce. The picrate is also sold under the name of 'spirit green.'

Döbner's process. This consists in heating dimethyl aniline with benzotrichloride in presence of metallic chlorides. It may be represented by the following equation:



$$C_6H_5.CCl_3 + 2C_6H_4.N(CH_3)_2 = 2HCl + {-}C\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_5\\C_6H_4N(CH_3)_2\ \ Cl\end{cases}$$

The following proportions are recommended by the patent:

3 parts dimethylaniline,
2 ,, benzotrichloride,
1·5 ,, zinc chloride,

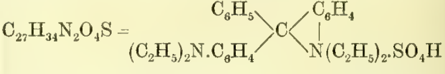
are to be heated for three hours to 110°C. in an enamelled iron vessel under constant stirring. The resulting melt is transferred into a still, and steam is blown through it to remove all excess of trichloride. It is then thoroughly extracted by boiling water. The filtrate is now precipitated by salt, and the precipitate recrystallised from water. This process, which always yields the zinc double chloride, is no longer in use, owing to its comparatively small yields.

The oxalate of benzaldehyde green forms large plates of an intense grass-green colour, which dissolve easily in hot water. It contains three molecules of oxalic acid to every two of green base.

The zinc double chloride, which has the composition $3(C_{23}H_{25}N_2Cl) + 2ZnCl_2 + 2H_2O$, forms green crystals with a fine yellow metallic lustre. It is not quite so easily soluble as the oxalate.

The application of these salts is similar to that of all the basic dye-stuffs, and need not here be described.

3. *Brilliant green.* (Syn., *Ethyl green*, *Emerald green*; also all the other names given for the preceding compound, with the addition of the letters G, J, or Y (meaning *gelb*, *jaune*, or yellow).



$$C_{27}H_{34}N_2O_4S = \begin{matrix}C_6H_5\\(C_2H_5)_2N.C_6H_4\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}C_6H_4\\|\\N(C_2H_5)_2.SO_4H\end{matrix}$$

is prepared from diethylaniline by exactly the same process as described for benzaldehydic green. After precipitating the free green base, it is transformed into its sulphate by mixing it with the theoretical quantity of sulphuric acid diluted with its own weight of alcohol. The mixture forms a thick tar at first, but suddenly solidifies into a mass of well-defined crystals.

The shade of this green is considerably yellower than that of the ordinary benzaldehyde green.

4. **Victoria green** 3 B, $C_{23}H_{23}N_2Cl_3$. This is a colouring matter prepared from dichlorobenzoic aldehyde instead of the ordinary benzoic aldehyde. It is considerably bluer in shade than the ordinary benzaldehyde green.

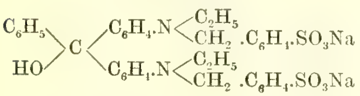
Acid greens. Considerable importance has always been attached by dyers to the sulpho-derivatives of basic colouring matters, because these are more easily and evenly dyed on wool than the hydrochlorides and other salts of the bases themselves. Many attempts have, therefore, been made to obtain acid greens. They were at first only partly successful; at present there are, however, several acid greens in commerce, ranging in shade from a yellowish green to a clear greenish indigo blue. They are very largely used in wool dyeing, especially for mixed shades.

The oldest of these acid greens, which appeared in the market in 1878, was called

5. **Helvetia green** or **Acid green C**. It was the sodium salt of the mono-sulpho- derivative of the ordinary benzaldehyde green, prepared either by sulphonating the green itself by means of sulphonyl chloride SO_3HCl, or by sulphonating tetramethyldiamidotriphenylmethane and oxidising the resulting colourless acid by means of plumbic peroxide. Neither of these two methods works satisfactorily. For this reason the product has gradually been abandoned, and replaced by the benzyl derivatives now to be described, which are more easily prepared, and at the same time much more brilliant in shade.

6. **Benzyl acid greens.** In the various attempts to prepare acid greens the great reluctance of the phenyl groups, combined with the central carbon, to the entrance of the sulpho- group was noticed. This reluctance is, indeed, quite characteristic of all triphenylmethane derivatives. It is the cause of the difficulties experienced in preparing sulphonated derivatives of these dye-stuffs. It was, therefore, a happy thought to introduce into the molecule of the green an independent radicle, capable of receiving the sulpho- group without influencing more than necessary the shade and other properties of the green. Such a radicle was found in the benzyl group. If we introduce this, instead of methyl and ethyl, into the amido- groups of the green, it acts in the manner of a radicle of the fatty series, influencing the shade of the green very little. The C_6H_5- group, however, brought into the molecule as a constituent of the benzyl radicle is capable of being sulphonated with the greatest facility. Various dye-stuffs have been prepared according to this principle. Of these *Guinea green B* is the simplest. It is the disulpho- derivative of diethyl dibenzyldiamidotriphenyl carbinol

$C_{37}H_{36}N_2O_7S_2Na_2$:



obtained by combining benzaldehyde with two molecules of ethyl benzylaniline sulphonic acid, and oxidising the leuco-compound thus obtained. This product was discovered by G. Schultz and Streng, 1883, and patented (Germ. Pat. 50782, April 9, 1889; Eng. Pat. 7550, 1889). It is an excellent and very useful dye-stuff. *Guinea green B V*, which dyes a more yellowish shade, is obtained in the same manner, using metanitrobenzoic aldehyde instead of the ordinary benzoic aldehyde.

The various shades of *light green* or *acid green* sold by the majority of manufacturers are prepared somewhat differently. Benzoic aldehyde is combined with two molecules of benzyl-methyl or benzyl-ethyl aniline. The base thus obtained is treated with sulphuric acid, when *three* sulpho- groups enter the molecule, one of which is linked to the phenyl radicle containing no amido- group, whilst the two others are combined with the benzyl radicles. The resulting trisulpho- derivatives are oxidised in the usual manner, yielding the dye-stuffs in the shape of a very soluble green powder.

7. A curious product, belonging to the class of acid greens, was described by R. Meldola, under the name of *Viridin* (C. J. 1882, 187; B. 14, 1385). It was prepared by oxidising benzyl diphenylamine, and sulphonating the resulting green, soluble in spirit. This green, or a substance very similar to it, had already previously been prepared by Ch. Girard (Wurtz, Progrès de l'Ind. des Mat. col.; Paris, 1876; p. 134).

8. Another *green*, belonging perhaps to this class of substances, is the *azo- green* discovered by Sohst and Runkel, patented and manufactured by the Farbenfabriken vorm. Fr. Bayer and Co. of Elberfeld (Germ. Pat. application F 4454). It is obtained by diazotising metamido-tetramethyl-diamido-triphenylmethane, re-acting with the resulting diazo-compounds on salicylic acid and oxidising the resulting azo- compound. The constitution of this substance has not yet been definitely established.

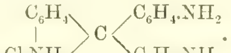
9. **Patent blue**, a product of the Farbwerke vorm. Meister, Lucius und Brüning, in Höchst-am-Main. This is a dye-stuff closely allied to the acid greens. It was discovered by Hermann, and patented by the Farbwerke (Germ. Pat. 46384 of Aug. 18, 1888, and many additional patents). It is prepared by a somewhat complicated method. Metanitrobenzoic aldehyde is combined with two molecules of dimethyl aniline. The resulting base is reduced, the amido- derivative diazotised, and, by boiling with water, transformed into meta-oxytetramethyldiamidotriphenylmethane. This is sulphonated by a treatment with sulphuric acid. The resulting sulpho- derivative is oxidised and transformed into a calcium salt, which is delivered into the market.

This dye-stuff dyes wool and silk a beautiful greenish blue of great brilliancy and clearness.

(B) *Derivatives of triamidotriphenyl methane.* This group contains some of the oldest artificial dye-stuffs, which were prepared by strictly empirical methods. When the constitution of the triphenylmethane group was discovered, synthetical methods for producing dye-stuffs of this group were gradually introduced. At the present time the old empirical processes hold their own for the production of the old colouring matters, whilst the synthetical methods, which are mostly patented, are used for preparing new dye-stuffs of great beauty and perfection.

The prototype of this group is—

1. **Parafuchsine**, the anhydrochloride of triamidotriphenylcarbinol $C_{19}H_{18}N_3Cl$, the constitution of which is:



It always crystallises with four molecules of water of crystallisation, which should be added to the above formula.

This is the dye-stuff which was used by O. and E. Fischer for the elucidation of the chemistry of all this class of substances (O. and E. Fischer, A. 194, 1878, 242; B. 11, 1079; 13, 2204). It is one of the oldest artificial dye-stuffs; it was discovered in 1858 by A. W. Hofmann (J. 1858, 351); and re-discovered by Rosenstiehl in 1869 (Bull. de la Soc. Ind. de Mulhouse, vol. 36, p. 264). For a long time it was considered a substance of merely theoretical interest, because its shade is almost identical with that of ordinary fuchsine or magenta (see under 2), which is much more easily prepared. At present, however, it is manufactured on a large scale, not as a dye-stuff for sale, but as a raw material for certain blues, which will be mentioned later on.

A large number of reactions have been observed and described, which result in the formation of pararosaniline. Of these the following may be mentioned:

(*a*) Pure aniline heated with carbon tetrachloride yields parafuchsine. This method was practically used on a manufacturing scale by Monnet and Dury in Lyons.

(*b*) Pure aniline, heated with iodoform, gives a fair yield of parafuchsine iodohydride.

(*c*) Pure aniline, heated with paranitrobenzylic chloride in the presence of iron filings or iron salts gives a good yield of parafuchsine. This method, or modifications of it, form the substance of Greiff's and Baum's patents (Germ. Pat. No. 15120 and 19304 Greiff, and 41929 Baum).

(*d*) Pure aurine (rosolic acid), which will be described later on, yields parafuchsine if strong ammonia be allowed to act on it for a long time at a high temperature.

(*e*) It has been shown (*v.* introduction) that the reduction-product of parafuchsine is paraleuco-aniline, and that the latter is identical with triamidotriphenylmethane. The latter may easily be prepared from triphenylmethane by nitration and reduction, and by various other methods. Attempts have not been wanting to work out a method for the production of parafuchsine from synthetical leucaniline. No good method, however, has hitherto been discovered for this purpose, and all the patents based on this reaction have proved failures. It is very easy to produce a trace of fuchsine in a solution of leucaniline; but no method is known for finishing the reaction.

(*f*) Mixtures of pure aniline with pure paratoluidine yield parafuchsine if subjected to oxidation. This is the usual practical way for the production of parafuchsine. The oxidation may be effected either by arsenic acid or by nitrobenzene. Other oxidising agents—such as mercuric bichloride, stannic tetrachloride, &c.—produce the same result, but at a higher cost. The arsenic acid process (which will be described later on) is almost exclusively used for the production of parafuchsine. The chemical reaction which takes place is very simple. Arsenic acid is reduced to arsenious acid. The oxygen which is thus obtained combines with hydrogen of the aromatic bases:

$$2C_6H_5NH_2 + C_6H_4.CH_3.NH_2 + 3O = 2H_2O + \underset{\text{Triamidotriphenyl carbinol.}}{C_{19}H_{18}N_3OH}$$

The methyl group of paratoluidine is used up for producing the central carbon around which the other radicles are grouped.

(*g*) Diamidodiphenylurethane, mixed with aniline and heated with oxidising agents, yields parafuchsine. This synthesis forms the basis of a new manufacturing process.

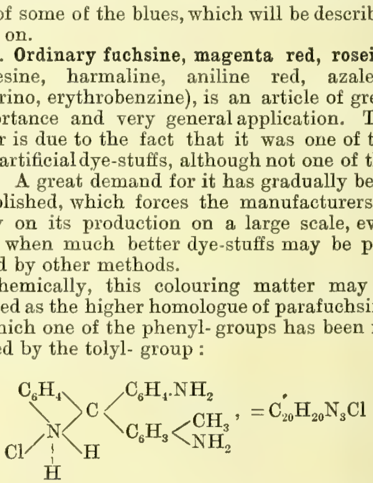
It has already been said that parafuchsine has no advantages over ordinary magenta red for dyeing purposes. It is, therefore, never to be met with in the market. As a rule the melts are worked up in the same manner as ordinary magenta melts, but the resulting crystals of the pure hydrochloride are re-dissolved and precipitated in the shape of pararosaniline base by the addition of ammonia or milk of lime. The base is then used for the production of blues.

Parafuchsine hydrochloride forms small glistening crystals of metallic green lustrous colour. As a rule, they are very small, much smaller than the crystals of the ordinary magenta. Parafuchsine acetate is similar in appearance and crystallises much more easily than the ordinary magenta acetate.

Pararosaniline is important, because it is the parent substance of all the various violets, and of some of the blues, which will be described later on.

2. **Ordinary fuchsine, magenta red, roseine** (rubesine, harmaline, aniline red, azalein, solferino, erythrobenzine), is an article of great importance and very general application. The latter is due to the fact that it was one of the first artificial dye-stuffs, although not one of the best. A great demand for it has gradually been established, which forces the manufacturers to carry on its production on a large scale, even now, when much better dye-stuffs may be prepared by other methods.

Chemically, this colouring matter may be defined as the higher homologue of parafuchsine, in which one of the phenyl- groups has been replaced by the tolyl- group:



Ordinary fuchsine.

The product of commerce, though chiefly composed of this substance, invariably contains an admixture of parafuchsine as well as of the higher homologues $C_{21}H_{22}N_3Cl$ and $C_{22}H_{24}N_3Cl$. Like parafuchsine, it contains four molecules of water of crystallisation.

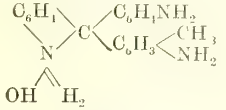
Fuchsine is invariably prepared by oxidising a mixture of aniline with para- toluidine and ortho- toluidine. This mixture is generally known as 'aniline for red,' and was originally produced by the nitration and subsequent reduction of a certain fraction of crude benzene, which consisted of benzene and toluene. Sometimes it even contained some xylene; in this case xylidine entered into the composition of 'aniline for red.' At present most of the 'aniline for red' is a mixture of pure aniline with crude toluidine. By the latter we mean the mixture of ortho- and para- toluidine which is obtained by the nitration and subsequent reduction of pure toluene. Crude toluidine consists as a rule of 60 p.c. ortho- toluidine and 40 p.c. para- toluidine. The quantity of aniline added to crude toluidine in order to produce the 'aniline oil for red' varies according to the recipes of various manufacturers. As a rule, half of the weight of the toluidine is added. A certain boiling-point (for instance, 188–200°) and a certain specific gravity (for instance 1·010) are prescribed, and should be strictly adhered to by the aniline oil manufacturer. In some cases an addition of xylidine is necessary in order to produce a product of the necessary boiling-point and density. Theoretically, an oil containing equal molecules of the three bases would be required; but for practical work an excess of aniline and ortho-toluidine is required, because a part of these two escapes the reaction, whilst the para- toluidine is entirely used up.

Of all the methods which in the course of time have been proposed for oxidising this mixture, only two have survived, both having their special advantages. They are known under the names of the *arsenic acid melt* and the *nitrobenzene process.*

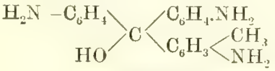
Magenta was originally prepared by Natanson, in 1856, by heating aniline with ethylene chloride. In 1858 Hofmann observed its formation when allowing carbon tetrachloride to act on aniline. In 1859 Verguin prepared it by the action of stannic chloride on aniline. Verguin's employers, the dyers Renard Frères and Franc, in Lyons, took up its manufacture on a large scale, and invented the name *fuchsine.* Later on a company was formed, under the name of 'La Fuchsine,' for working Verguin's patent. Gerber-Keller invented a process for oxidising aniline by means of mercuric nitrate. The dye-stuff thus obtained was believed to be different from fuchsine, and received the name *azaleine.* In 1860 Medlock discovered the arsenic acid process, which is still in actual use. His patent was invalidated owing to a clerical error contained in the description. In 1869 Coupier described his process for producing fuchsine by the nitrobenzene process. This method, which did not give good results at first, was gradually worked out by various manufacturers, and is now equivalent, if not superior, to the arsenic-acid process.

Various salts of rosaniline were formerly in commerce. The original fuchsine was the hydrochloride, azaleine was the nitrate; whilst magenta and roseine were the names applied to acetate, produced by Nicholson, the first to manufacture this colouring matter in a practical and rational manner. Gradually the nitrate and acetate disappeared from the market. At present the hydrochloride is the only salt produced, to which, therefore, the original name of fuchsine should be applied. English manufacturers still use the names magenta and roseine for the hydrochloride. A large quantity of the fuchsine manufactured is transformed into rosaniline, which is delivered into the market either under this name or as 'magenta base,' 'red base,' or 'roseine base.' These names are not quite correct, because rosaniline may not strictly be considered as the true base of the hydrochloride of fuchsine.

The true base of fuchsine is



which, in the moment of its formation, undergoes a molecular transformation into



Rosaniline
(Triamidodiphenyltolylcarbinol).

Manufacture of fuchsine.

1. *Arsenic acid process.* The properties of the 'aniline oil for red' have already been discussed. The mixture of bases known under this name is transformed into the dye-stuff by heating it with arsenic acid. The latter is prepared by oxidising arsenious acid (white arsenic) by means of nitric acid in closed earthenware pots. The escaping nitrous fumes are condensed in a tower, in which they meet an opposing current of water and air. The nitric acid is thus regenerated, and may be used again. Practically, therefore, the formation of the arsenic acid is accomplished by the oxygen of the air. The arsenic acid solution obtained has a sp.gr. of 1·85–2·3, and contains from 60–75 p.c. of arsenic acid H_3AsO_4. 1,500–1,700 kilos of this solution are required in order to oxidise 1,000 kilos of 'aniline oil for red.' These quantities of the reagents are introduced into cast-iron pots, closed by a lid; a mechanical stirrer and a tube for the escape of the vapours should be provided. The mixture is then gradually heated to 180°C. This temperature should be strictly maintained during the whole operation. If the temperature rise above 190°, the dye-stuff already formed is decomposed. From eight to ten hours are required in order to complete the reaction. During the whole time vapours escape, which should be condensed in a leaden coil connected with the escape tube, and cooled by a current of water. At first the distillate consists chiefly of the water introduced with the arsenic acid. Later on, the water formed in the reaction distils; at the same time some aniline oil goes over. The total quantity of the aniline escaping the reaction is one-third, or even one-half, of the quantity originally used. The melt, which is very thin at first, gradually becomes viscid; at the same time it assumes a brown, metallic lustre. Samples should be taken from time to time. When the melt becomes brittle on cooling, the reaction is finished, and the fire should be drawn. The melt is then at once removed from the pot. In some factories an opening is provided for this purpose in the lowest part of the pot, which is closed by a lid and screw whilst the heating lasts. As a rule, however, it is preferred to remove the cover of the pot, and to ladle out the melt. The latter is spread on trays made of sheet iron. On cooling, it solidifies into cakes, which are very brittle, and break up into small lumps on being handled.

The crude melt contains the colouring matter in the shape of arsenite, together with an excess of arsenious and arsenic acids, some coloured by-products (*v. infra*), and a large quantity of tarry impurities. In order to obtain the pure dye-stuff, the crude melt is introduced into horizontal wrought-iron boilers, in which an eccentric horizontal stirrer is made to rotate. Water is added, the lid of the boiler is closed, and steam is introduced at a pressure of four to five atmospheres. After several hours' vigorous stirring, the greater part of the rosaniline arsenite has been dissolved by the water. The liquid is then forced through felt into iron tanks, where it is allowed to cool down to 50°C. A sufficient quantity of salt is then added to precipitate the whole of the colouring matter. By the addition of the salt a mutual decomposition takes place. Sodic arsenite is formed, and remains in the liquid, whilst the colouring matter is precipitated in the shape of chloride. It settles out as a thick green tar of metallic lustre, which solidifies into a brittle substance on cooling. The supernatant aqueous liquid is then drawn off, the crude fuchsine is chipped out, and introduced into another extractor, similar to the one used for treating the melt. A very small quantity of soda ash or chalk (about $\frac{1}{2}$ p.c. of the weight of the crude dye-stuff) is added, and a second extraction takes place. The liquid is again forced through felt into large wooden vats, in which some wooden boards are suspended. When the vats are filled, a small quantity of hydrochloric acid and clean butter-salt is added to each vat. In these vats the dye-stuff separates out, in the shape of fine glistening green crystals. The largest crystals are generally deposited near the surface of the liquid. When the crystallisation is finished, the mother-liquor is drawn off, and the crystals are collected and sorted according to their shape and size. The largest crystals are sold under the name of 'diamond fuchsine.'

By-products. The residues of the first boiling may be subjected to a second extraction; as a rule, some hydrochloric acid is added in this case. A deeply-coloured solution is thus obtained, from which an impure colouring matter may be precipitated by the addition of salt. This colouring matter is sold under various names (magenta cake, cerise, grenadine, marroon), and finds a ready market. It dyes a magenta colour, which is less brilliant than the shade obtained with the crystals. A third boiling is sometimes necessary. The colouring matter obtained from this is very impure. It is, therefore, dissolved in weak hydrochloric acid, and some zinc-dust is added, which reduces the magenta contained in the liquid. On precipitating with salt, a colouring matter of a brown shade is obtained, which is sold as 'Nangking,' or 'leather brown.' The black insoluble residue of the third boiling still contains some dark-blue colouring matters of the induline series, which are, however, not worth the trouble of extracting.

The mother-liquors from the crystals contain a yellow colouring matter of great fastness and purity. This substance, known under the name of *phosphine*, belongs to another group of dye-stuffs, being a salt of diamidophenyl acridine. For extracting it from these mother-liquors, the latter should be acidulated with hydrochloric acid, and some zinc-dust added until all the fuchsine is reduced. The phosphine may then be precipitated by the addition of sodic nitrate. The amount of phosphine formed varies according to the composition of the aniline oil and the temperature of the melt. It is never considerable, and very often the quantity present is so small that it is not worth while to separate it.

Recovery of the arsenious acid. Formerly the residues of the manufacture of magenta were left in the factory yards or thrown into the sea. At present this is not allowed, and the manufacturers are invariably forced to recover their arsenious acid, so as to prevent the poisoning of wells and streams. The recovery, as it is now carried out, is so economical that the value of the arsenious acid obtained covers the cost of working the process. The process, which was worked out by A. Leonhardt, consists in burning the solid residues and using the heat for evaporating the arsenical liquids. The dry residue of the evaporation is introduced into the furnace, and burned along with the solid residues. Care is taken to introduce no more air than is necessary for burning the organic matter. By this precaution a complete volatilisation of the arsenic in the metallic state is obtained. The vapours of arsenic are led into a highly-heated combustion-chamber. Here they are mixed with the necessary quantity of hot air to completely burn the metallic arsenic into arsenious acid As_2O_3. The vapours of the latter are then led through condensing chambers similar to those used in the manufacture of white arsenic. In these chambers the arsenious acid is deposited in the shape of a white powder. From time to time the chambers are opened, the arsenic is removed, and used again for the manufacture of syrupy arsenic acid by the aid of nitric acid. A certain stock of arsenic is thus sufficient to carry on the manufacture of fuchsine for an indefinite period.

2. *The nitrobenzol process.* This process was originally invented by Coupier, of Paris; but it was for the first time successfully worked on a large scale by the firm of Meister, Lucius und Brüning, of Höchst-am-Main. Other firms followed in the course of time, and at present this process is more frequently used than the one with arsenic acid.

It was originally supposed that the nitrobenzene used in this process enters into the rosaniline formed, after having served as an oxidiser. At present it is generally recognised that the nitrobenzene merely acts as an oxydising agent, and that it is transformed into tarry matters, which are useless and remain in the residues. The nature of the nitro- compound used is, therefore, of no influence on the composition of the dye-stuffs obtained. Pure nitrobenzene, or a mixture of nitrobenzene with nitrotoluene, may be used. Ortho-nitrotoluene acts more easily than any other nitro- compound; it has, therefore, been used with advantage by the writer. Para-nitrotoluene has little tendency to act as an oxidiser. If, therefore, a mixture of nitrobenzene with the two nitrotoluenes (the so-called 'nitrobenzol for red') be used, the para-nitrotoluene escapes with the distillate.

The advantage of the nitrobenzol process consists, therefore, not in an economy of ingredients, but in the fact that by its application magenta free from arsenic may more easily be btained. The yield in good crystallised fuch-ine is slightly larger (if only the aniline used e taken as basis of the calculation) than in the rsenic acid process. This increase of yield pays or the increased price of the oxidising agent. n times when commercial benzol is cheap the rocess compares favourably with the arsenic cid process, whilst it is at a disadvantage when he prices of benzol are rising. For working his process it is a condition that the manu-acture of aniline be carried on in the same orks; the distillates are a mixture of aniline nd nitrobenzene, which must be returned into he reduction process before they can be used gain.

The process is worked with different propor-ions and in a different manner in different orks. It is based on the following facts: Aniline nd nitrobenzene do not react upon each other; or does a reaction take place if aniline hydro-hloride be added. But if a small quantity of on chloride be added, a reaction sets in, at a emperature 160°. If the aniline and aniline alt used are pure, a dye-stuff of the induline roup is obtained; but if para-toluidine and rtho-toluidine be present in the necessary pro-ortions ordinary fuchsine is the result of the eaction. The oxidising influence of the nitro-ompound, however, attacks also the fuchsine lready formed, and part of it is therefore ecomposed again. For this reason, quantitative ields cannot be obtained. At 190° the action f the nitrobenzene becomes so violent that all e colouring matter is destroyed. The greatest are is, therefore, required in this process, and e temperature should never be allowed to rise ver 175°. Cold-air flues, and even arrange-ents for cooling with water or ice, are therefore variably provided in connection with the elting-pots. The size of the latter has been nstantly increased, because it is easier to keep rge vessels at a constant temperature than nall ones. Enormous pots, capable of working e or two tons of melt, have been used. Excel-nt arrangements for stirring should be provided. is a good plan to make the melting-pots of herical shape, and to give the stirrer an lique position in this spherical pot. No water ould be present in the mixture, as in this case e nitro- compound is simply reduced into iline by the iron protochloride, and the reac-on stops. The hydrochloric acid used should, erefore, be combined with the necessary quan-ty of the aniline and the mixture evaporated ntil it solidifies into 'aniline salt cake' on oling. Sometimes the iron chloride solution added, so that the cake obtained is intimately ixed with the iron salt. This cake is then ssolved in the rest of the aniline, the nitro-mpound is added, and the mixture is heated ntil the reaction sets in. Other manufacturers efer to add iron filings or dry ferrous chloride the mixture of aniline with aniline cake and trobenzene. An ingenious patent, taken out Herran and Chaudé, proposed the use of rtain double salts of the general formula $_2Cl_6,2RCl_2$, such as ferri-ferrous chloride, ferri-nc chloride, alumini-zinc chloride, and others. he addition of iron filings, originally proposed Coupier, is not customary at present. Anhy-ous zinc chloride, which has also been proposed as a means of starting the oxidising action of the nitro- compound, has not proved satisfactory.

The following proportions have been proposed:

100 parts aniline for red,
50 ,, nitrobenzene,
3–5 ,, iron filings,

and a sufficient quantity of hydrochloric acid to neutralise two-thirds of the aniline (Häussermann). The quantity of nitrobenzene is too large; it may very well be reduced to 40 parts, or even less.

Wurtz gives the following proportions:

38 parts aniline,
17–20 ,, nitrobenzene,
18–22 ,, hydrochloric acid,
2 ,, iron filings.

The following is Coupier's mixture:

67 parts toluidine,
95 ,, nitrotoluene,
65 ,, hydrochloric acid,
7 ,, ferrous chloride.

The large quantity of nitrotoluene proposed in this prescription is due to the fact that only the ortho-nitrotoluene, of which about 50 parts are present in the mixture, acts as an oxidiser. The para-nitro- compound is recovered in the distillate.

The following proportions were used by the writer in regular factory work:

400 kilos aniline for red,
222 ,, hydrochloric acid, 20°Bé.,
247 ,, orthonitrotoluene,

and the ferrous chloride prepared from

9 kilos iron borings, and
41 ,, hydrochloric acid.

Half of the aniline is dissolved in the 222 kilos of hydrochloric acid, the solution of the ferrous chloride is added, and the whole evaporated in a stone still before being mixed with the remainder of the aniline and the nitrotoluene.

The nitrobenzene melt cannot be pushed so far as the arsenic acid melt. When finished it should not solidify into a brittle mass on cooling. It should be still soft, owing to a proportion of uncombined aniline which it still contains. This aniline must be extracted by boiling up with a small quantity of dilute hydrochloric acid. After its removal, the melt becomes brittle on cooling. It is worked up in the Leonhardt extractors, in exactly the same manner as described for the arsenic acid melt.

Recent improvements. It has already been said that several synthetical methods have been proposed for the manufacture of magenta, which met, however, with no success. Quite recently improvements have been introduced into the old melting processes, which, being based on theoretical considerations, promise well for the future. The most important of these improvements is the one described in the German patent 53937 (and additional patent) of the Farbwerke vorm. Meister, Lucius und Brüning in Höchst-am-Main, dated November 27, 1889. It consists in replacing, in the nitrobenzol process, the aniline for red by a mixture of diamido-diphenyl-methane and aniline. The patents refer only to the production of the diamido-diphenyl-methane, which is prepared by first acting with formic aldehyde (now an article of commerce) upon aniline. The anhydroformaldehyde aniline obtained is heated with aniline and aniline hydrochloride, by which means diamido-diphenylmethane is easily formed. If instead of $C_6H_5N.CH_2$, anhydroformaldehyde aniline, any of its higher homologues be heated with the corresponding bases, the homologues of diamido-diphenylmethane are produced. By introducing these bases instead of paratoluidine into the magenta melt, very large yields of the dye-stuff are said to be obtained. The dye-stuff prepared by this new method is sold under the name of 'Neu-Fuchsin' (new magenta).

Quite recently a patent has been applied for by Cassella & Co., of Frankfurt-am-Main, the essence of which is probably the same. It consists in introducing methylic alcohol into the arsenic acid melt. Formic aldehyde is probably thus produced, which is at once transformed into diamidodiphenylmethane.

Acid magenta. The ordinary fuchsine or magenta has been used for dyeing cotton, wool, and silk. But its properties make it necessary to use neutral or very slightly acid baths. This is a considerable drawback to its use on silk or wool, especially in combination with other dye-stuffs which require distinctly acid dyebaths for their successful application. It was, therefore, a decided progress to introduce a sulpho- derivative of magenta into the market. This progress was realised by H. Caro in 1877 (Eng. Pat. 3731, 1877; Germ. Pat. Badische Anilin- & Soda-Fabrik, No. 2096). He proved that magenta, which shows a marked resistance to ordinary sulphuric acid, may easily be converted into a trisulpho-derivative by treatment with fuming sulphuric acid. The ordinary crystallised hydrochloride is used. It is introduced in a finely-powdered condition into fuming sulphuric acid; the mixture is then heated to a temperature not below 120° and not above 170°C. Hydrochloric acid is given off, and the sulpho- derivative is formed. When the operation is finished, it is diluted with water and worked up in the usual manner, by first preparing the lime-salt and then converting it into the sodium salt. The para- derivative has the composition $C_{19}H_{16}N_3O_{10}S_3Na_3$, the higher homologue $C_{20}H_{18}N_3O_{10}S_3Na_3$; the ordinary acid magenta is a mixture of the two. It forms a metallic green powder, very soluble in water with magenta colour, which disappears completely on addition of caustic alkali, the sulpho-derivative of the colourless triamido-triphenyl carbinol being formed.

Acid magenta may also be obtained by acting with chlorosulphonic acid SO_3NCl upon dry magenta base (E. Jacobsen, Germ. Pat. 8764, 1879; Eng. Pat. 2828, 1879).

By using the various by-products of magenta instead of the pure dye-stuff, acid derivatives of these may be obtained which prove particularly valuable for dyeing mixed shades.

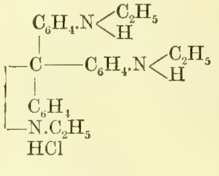
Magenta base (red base, roseïne base). A large proportion of the fuchsine produced is transformed into the corresponding base, the composition of which has already been discussed. For the production of a good base, crystallised fuchsine only should be used. This is dissolved in a large bulk of boiling water, and basified either with milk of lime or with ammonia. No caustic alkali should be used. From the filtered solution the base settles out on cooling in crystals, which have the shape of a fern-leaf of pale-pink colour. In the air they generally become darker, because a certain amount of magenta carbonate is formed on their surface. The base thus prepared is sold for conversion into violets and blues (*q. v.*).

Colouring Matters derived from Rosaniline.

The famous researches of A. W. Hofmann proved, at an early period, that rosaniline is capable of having the hydrogen atoms of its amido- groups replaced by alkyl groups, and that the substances so formed are remarkable not only for the brilliancy, but also for the great variety, of their shades. Hofmann himself introduced the alkylic radicles of the fatty series into the molecule of rosaniline, and thus obtained the colouring matters which for a long time played an important part under the name of Hofmann's violets. Girard and De Laire discovered a method of introducing the phenyl and other aromatic groups into the molecule of rosaniline, and thus inaugurated the manufacture of aniline blues. It was then attempted, first by Lauth, to produce alkylated rosanilines by direct oxidation of alkylated aniline, and this method proved of great practical importance in the hands of Bardy, although the theory of this process was only understood at a much later period. Finally, a synthetical method for the production of certain alkylated rosaniline derivatives which cannot be produced by direct alkylation of rosaniline itself, was discovered by Kern, whose processes are based on the theoretical researches of Michler.

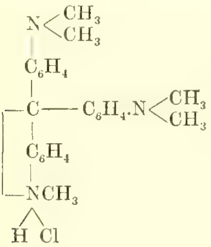
All these colouring matters will now be described, and the methods of their formation discussed.

1. **Hofmann's violet** $C_{26}H_{32}N_3Cl$, hydrochloride of triethyl rosaniline:



is obtained by heating magenta base with ethylic iodide, bromide, or chloride, and a sufficient quantity of alcoholic soda solution to neutralise the acid formed in the reaction. The magenta base is prepared by decomposing a very weak fuchsine solution with milk of lime or ammonia. From the filtered solution the base crystallises in small leaflets of a pink colour. The alkylation is effected in closed vessels of copper or cast-iron, which are heated to 80–100°C. by steam or in a water-bath. The trimethyl rosaniline hydrochloride, which is slightly bluer in shade, was formerly also prepared. This is no longer employed. By using less of the alkyl haloids than is necessary for completing the reaction, redder shades were obtained, which were mixtures of the mono- and diethyl- or methyl-rosanilines.

2. **Methyl violet B.** C. Lauth, wishing to find a new method for the production of Hofmann's violets, tried to oxidise methylated aniline. He obtained a violet of much bluer shade. Bardy worked out the method, which was patented by Poirrier and Chappat (French Pat. 71970, dated June 16, 1866). The product obtained was proved to be the hydrochloride of pentamethyl rosaniline $C_{24}H_{28}N_3Cl$:—



This dye-stuff, which became of enormous importance, was for a long time known under the name of *Violet de Paris.*

The mode of formation is very interesting. Many researches have shown that it is best prepared from pure dimethyl aniline, which should be as free as possible from every trace of monomethyl aniline. If three molecules of dimethyl aniline be oxidised into one molecule of the dye-stuff, one of the six methyl groups present serves to form the central carbon atom, whilst the other five remain combined with the amido- groups of the dye-stuff formed.

The process of oxidation employed is totally different from those resorted to in the manufacture of magenta or fuchsine. Cupric chloride is used as an oxidiser at a temperature which is little above that of the atmosphere. The cuprous chloride formed is again transformed into cupric salt by the oxygen of the air. The air should, therefore, have easy access to the mixture. To fulfil this condition, a porous condition is given to the melt by the admixture of sand or other indifferent materials. Cakes are formed of the mass, and these are left on trays in a hot chamber. The following proportions have been recommended:

100	parts	sand,
10	,,	dimethylaniline,
3	,,	cupric nitrate,
2	,,	sodic chloride,
1	,,	weak acetic acid.

The cakes, which show a dull greenish colour at first, gradually assume a bronze lustre and become hard and brittle. They now contain the violet formed in an insoluble combination with cuprous chloride. To obtain the violet, the cakes should be powdered, and all soluble substances extracted with water. The double salt of violet and cuprous chloride should then be decomposed. Various means have been adopted for this purpose.

The original process consists in treating the material with a weak solution of sodic sulphide. Insoluble copper sulphide is formed, and the free violet is dissolved. From the filtered solution it may be precipitated by the addition of salt. It comes out in the shape of a gold-coloured tar of metallic appearance, which is collected and dried in jacketed pans. When dry it forms a brittle mass of metallic aspect, showing no tendency whatever to crystallise. It is sold under the name of 'Methyl violet B' or 'direct violet.'

The use of sodic sulphide has this inconvenience, that every excess of reagent acts as a reducing agent on the violet, transforming it into its leuco- compound, which cannot be separated from the violet, and impairs its strength, besides producing other inconveniences. To remedy this drawback, several factories adopted gaseous hydrogen sulphide instead of the sodium compound. Hydrogen sulphide has no reducing action on violet in neutral or slightly acid solutions. The use of this gas on a large scale is, however, extremely dangerous, and frightful accidents, which happened repeatedly, have led to the abandonment of its use.

The following methods, which have not yet been published, admit of the extraction of the violet without the use of sulphides.

The first is based on the fact that, although the violet combines with cuprous chloride in the shape of its hydrochloride, the same is not the case if the two be present as sulphates. If, therefore, the crude insoluble melt is boiled with dilute sulphuric acid, the violet goes into the solution together with the copper. The solution is then filtered off from the sand. If now salt were added in order to precipitate the violet, the insoluble compound would be re-formed. To prevent this, sodic sulphate (free from chloride) is used for precipitating the violet, which comes out as sulphate, whilst the copper remains in the solution. The violet sulphate is now carefully washed, re-dissolved, and re-precipitated in the shape of chloride by the addition of common salt.

Another process, which gives equally good results, is based upon the fact that the insoluble compound becomes soluble if the cuprous chloride contained in it be oxidised into cupric salt. For this purpose the crude cake is triturated with a solution of ferric chloride. It is then filtered off and washed. The violet, which has become soluble, may now be extracted with water, and precipitated by the addition of salt.

Great improvements have been effected in the melt itself. First of all, it was recognised that the cakes, if left to themselves, were apt to lose too much dimethylaniline by evaporation; they also remained insufficiently oxidised in their interior. To obviate this, the use of bread-kneading machines was resorted to, through which a current of air was blown. This current was made to pass through a vessel containing sulphuric acid, after leaving the machine. Complete oxidation was thus obtained, whilst the evaporating base was recovered in the acid.

Later on, the quantities of the copper salt were reduced, and some potassic chlorate was added to the mixture. This yielded the necessary oxygen, the presence of a current of air became superfluous, and the evaporation of the base could be stopped by using closed vessels or kneading machines.

Another great inconvenience is the sand. It is necessary as a diluting agent, but in the after-operations it is very troublesome, being very heavy and producing great wear of the apparatus. It was, therefore, a great progress to use clean salt instead of sand. The salt is quite as indifferent as the sand, but after having done its duty, it may be easily removed by solution, leaving the insoluble compound of violet and cuprous chloride in the shape of a fine dark powder, which is admirably fitted for being worked up into soluble product.

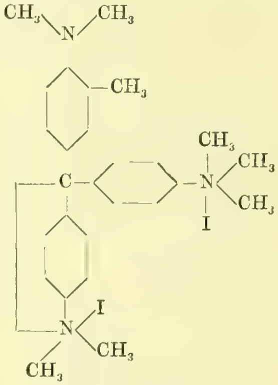
By such improvements it was possible to raise the yield of colouring matter, which at first hardly reached 45 or 50 p.c. of the dimethylaniline used, to 90 p.c. and more. If we remember that 30 p.c. of pure colouring matter are a fair yield in the manufacture of magenta, we may well understand that methyl violet, although manufactured from a much more expensive raw material than fuchsine, soon became much cheaper than its parent substance.

Quite recently the yields of violet have been further increased by a curious means. It consists in adding some phenol to the mixture. The action of the phenol, which may be recovered, is not quite clear, but by its use the yield of violet becomes very nearly theoretical.

In the manufacture of violet, especially by the older methods, there is always some tri- and tetra-methylrosaniline formed along with the penta-methyl derivative, because the methyl groups are attacked, and transformed into formic aldehyde, which escapes. The violet is, therefore, slightly redder than it ought to be. To compensate for this loss, Bardy treated his direct violet with benzylic chloride, and thus introduced benzyl groups wherever methyl was wanting. The violet of very blue shade thus obtained was brought into commerce under the name of *Methyl violet* 5 *B* or *Benzyl violet.* It has now lost its importance, having been to a great extent replaced by the very beautiful crystallised violets obtained by the synthetical method of Kern.

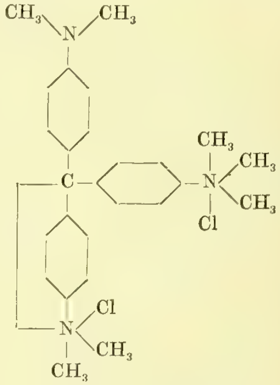
3. **Iodine green** and **Methyl green.** It has already been said that Hofmann's process of direct alkylation of rosaniline does not go farther than to the tri-alkyl derivatives. If the action of alkyl haloids be still continued, ammonium bases are formed. Thus Keisser obtained (1866), by heating Hofmann's violet with methylic iodide in a methylic alcohol solution, a green colouring matter, which was manufactured and sold for many years under the name of *iodine green.* A very similar dye-stuff was prepared from methyl-violet in a similar manner by Bardy, who used, however, methylic nitrate instead of the iodide. After several fearful explosions, the use of the nitrate was abandoned, and methylic chloride or bromide, also ethylic bromide, were used instead. The dye-stuff thus obtained was sold under the name of *methyl green.* It did not contain any iodine, and was therefore much cheaper than the iodine green, which it quickly replaced.

Chemically, the two may be considered as identical, viz. as methyl ammonium-derivatives of hexamethyl-rosaniline. Iodine green, being a derivative of ordinary rosaniline, of course contains one tolyl group:



Iodine green $C_{27}H_{35}N_3I_2$,

whilst methyl green is the corresponding derivative of pararosaniline:



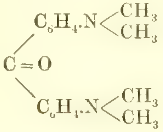
Methyl green $C_{26}H_{33}N_3Cl_2$.

Both these dye-stuffs were brought into commerce in the shape of their double salts with zinc chloride. The iodine green formed a dark powder, whilst the methyl green formed pretty green needles or leaflets.

To prepare these dye-stuffs the violets were simply heated with the alkyl haloids in closed enamelled iron vessels to 120°C. Some wood spirit, or common alcohol, was added as a solvent. A pressure of 10–12 atmospheres was observed, which went down when the reaction was finished. The crude product was dissolved in water. This solution was of dark-blue colour, because there was always some violet which remained unattacked. To separate this, the solution was shaken up with amylic alcohol, which dissolved out the violet. The green remained in the aqueous solution, from which it could be precipitated by the addition of zinc chloride and common salt. To obtain crystals, the crude green was re-crystallised from spirit.

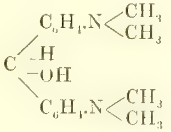
These greens have now almost entirely been replaced by the diamidotriphenylmethane derivatives already described, which are not only more brilliant in shade, but also much more stable. Iodine green and methyl green are decomposed, and turn a dirty violet even by the action of a gentle heat, as produced in cylindering tissues, and on many other occasions.

Pararosaniline derivatives prepared by Kern's method. A new way of preparing alkylated pararosanilines was indicated by Kern, who started from the observations published by W. Michler (B. 9, 1876, 716). This chemist had shown that by acting with carbonyl chloride $COCl_2$ upon dimethylaniline, the chloride of dimethylamidobenzoic acid is formed, which acts again on dimethylaniline, yielding tetramethyldiamidobenzophenone :



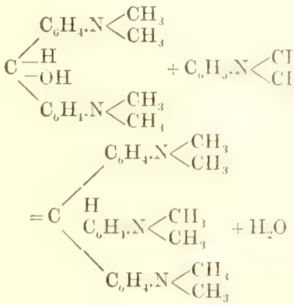
At the same time, so Michler observed, an intense blue colouring matter is formed. A. Kern (1883) followed up Michler's observations, and discovered not only the nature of the blue colouring matter, but also the conditions under which it may be obtained, as the sole product of the reaction. The colouring matter proved to be pure hexamethylpararosaniline, the formation of which is due to the action of another molecule of dimethylaniline upon tetramethyldiamidobenzophenone. This action is, however, not very energetic, and must be intensified by the addition of certain substances, or by substituting for the ketone certain of its more active derivatives. A number of various processes have thus been worked out, which will now be described.

A. Kern's original modification of Michler's experiment is based upon the fact that tetramethyldiamidobenzhydrol, the secondary alcohol derived from the ketone tetramethyldiamidobenzophenone, acts very easily upon aromatic bases, forming triphenylmethane derivatives. This process is described in Kern's Eng. Pat. No. 5450 (1883), and the corresponding Germ. Pat. Bad. Anilin- und Soda-Fabrik, No. 27032. Tetramethyldiamidobenzhydrol :



which had already been obtained by Michler by the action of sodium-amalgam upon the ketone, may, according to this patent, be prepared industrially by boiling a solution of the ketone in amylic alcohol with caustic soda and zinc-dust. When the reduction is finished, the alcohol is blown off with steam, the residue dissolved in hydrochloric acid, and purified by fractional precipitation with caustic soda.

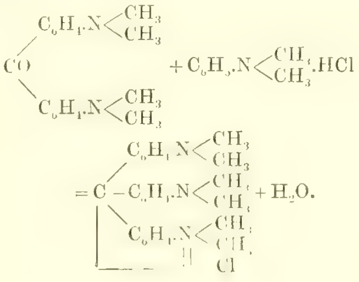
The product thus obtained may be condensed with primary, secondary, and tertiary aromatic bases, yielding in every case alkylated derivatives of paraleucaniline; thus, for instance, with dimethylaniline the leuco- base of hexamethylrosaniline is formed, if the two be brought together in a solution in weak sulphuric acid :



This leuco-base may be oxidised into the corresponding dye-stuff by the method indicated for the production of benzaldehyde green—viz. by the action of plumbic peroxide upon the hydrochloride of the leuco- base. The *hexamethylrosaniline hydrochloride* thus obtained is a beautifully crystallised substance, which forms green crystals if anhydrous, $C_{25}H_{30}N_3Cl$, or bronze-coloured prisms, if containing water of crystallisation. In the latter case, its composition is $C_{25}H_{30}N_3Cl + 8H_2O$. The great power of crystallisation of this substance is very remarkable, if we compare it with the ordinary violet obtained by direct oxidation of dimethylaniline, which, being a mixture of the tetra-, penta- and hexa- methylrosanilines, shows no tendency whatever to crystallise.

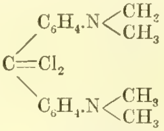
If in the process described diethyl aniline be substituted for dimethyl aniline, both for the production of the hydrol base and its subsequent transformation, the result is, of course, hexaethylrosaniline, which cannot be prepared by any other process. This product is manufactured and sold under the name of '*Ethyl-purple*, 6 *B*' (ethyl violet). It is a very beautiful colouring matter, dyeing fine bluish-purple shades.

Very soon a simpler method than the one described was discovered by Kern and Caro (Germ. Pat. 26016 and 29943 ; Eng. Pat. 4428, 1883). It was based upon the fact that the action of tetramethyldiamidobenzophenone upon dimethylaniline, which, in Michler's experiment, already had yielded a small amount of colouring matter, may be modified by the addition of certain substances, such as aluminium chloride, zinc chloride, and others. If these be present, the reaction of phosgene gas (carbonyl chloride $COCl_2$) upon dimethylaniline does not result in the formation of tetramethyldiamidobenzophenone ; this is only formed as an intermediate product, which reacts at once upon another molecule of the base, forming hexamethylpararosaniline :



The following is the method used at present for preparing *crystal violet* and *ethyl purple* 6 *B*: 100 kilos of dimethylaniline (or diethylaniline) are acted upon at a temperature of 20°C. with 18–20 kilos of carbonyl chloride; after twenty-four hours' standing another 50 kilos of the base and 30 kilos powdered zinc chloride are added. The mixture is now heated to 40–50°C., and 20 kilos more of the carbonyl chloride are introduced. After six hours' heating to 50°C., the reaction is finished. The mixture is now introduced into a still, basified with caustic soda, and the excess of dimethylaniline driven off with steam. The remaining base of the colouring matter is dissolved in weak sulphuric acid, and precipitated in the shape of its chloride by the addition of common salt. It is then recrystallised from water.

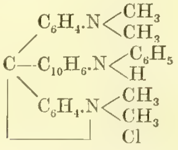
This process leads, of course, only to pararosaniline derivatives in which the three amido-groups are substituted in the same manner. Besides the hexamethyl- and hexa-ethyl derivatives, the trimethyltriphenyl derivative has been obtained from methyldiphenylamine (Amer. Pat. No. 327953, Kern and C. Müller). It was, therefore, a great progress when a method was found for effecting the condensation of tetramethyldiamidobenzophenone with all kinds of primary, secondary, and tertiary bases. This method, which was worked out by Kern and H. Caro, consists in the intermediate formation of the tetramethyldiamidobenzophenone chloride:



which, being much more active than the ketone itself, reacts most easily upon bases of every description. For the manufacture of colouring matters it is not necessary to isolate the chloride, an extremely unstable substance. It is sufficient to react with phosphorous trichloride upon a mixture of the ketone with the base which is to be introduced into the triphenylmethane derivative.

This process is described in the German Patent No. 277891, the English Patents No. 4850 and 5038 of 1884, and a large number of corresponding American patents, which contain many examples of its application to the production of dye-stuffs. Of these, however, only three have obtained lasting importance. These are basic colouring matters of a beautiful blue shade, and interesting because they are the only members of the triphenylmethane group which contain the naphthyl radicle.

Victoria blue B $C_{33}H_{32}N_3Cl$ has the constitutional formula:



It is prepared by mixing together

10 kilos tetramethyldiamidobenzophenone and

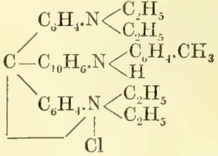
9 kilos α-naphthylphenylamine,

and adding

7 kilos phosphorous trichloride to the mixture.

The reaction, which sets in at once, is finished by heating to 110°C. The product is dissolved in water, and the solution precipitated with salt.

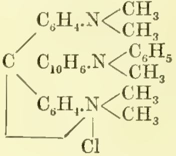
If α-naphthylparatolylamine be taken instead of the naphthylphenylamine, and condensed with tetra-ethyldiamidobenzophenone, a blue of a very greenish shade is obtained. It is sold under the name *night blue* (*Nachtblau*) and has the composition $C_{38}H_{42}N_3Cl$:



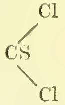
Another blue of very red shade is the one sold under the name *Victoria blue* 4 *R*

$C_{34}H_{31}N_3Cl$.

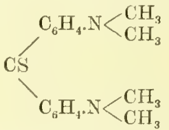
It is prepared from tetramethyldiamidobenzophenone and α-naphthylmethylphenylamine. Its constitution is probably



Many modifications of the processes here described have also been indicated and patented. Thus, instead of the carbonyl chloride, thiophosgene chloride

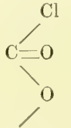


may be used, which yields with dimethylaniline the thioketone



The latter may replace the oxygen compound in all its applications.

Again, perchloro-formic ether



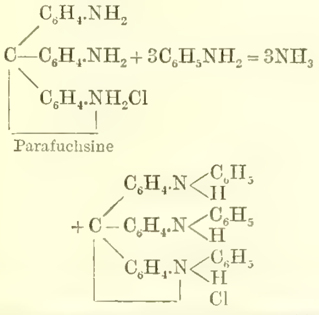
and similar substances have been proposed as substitutes for the phosgene chloride.

In the Germ. Pat. 34463, and the corresponding Eng. Pat. 4961 (1884), the Farbwerke Höchst vorm. Meister, Lucius, und Brüning describe a process for the production of mixed triphenylmethane colouring matters, which is substantially identical with those already described. It consists in reacting with dimethylamidobenzoic chloride, or analogous substances, upon tertiary aromatic bases. It is chiefly used for producing the 'Höchster Neublau' from methyldiphenylamine.

Rosaniline blues or phenylated rosanilines. These are of great importance, forming by far the majority of blue aniline dyes in the market. The chemistry of these compounds is, however, extremely complicated. The blues delivered into commerce are not chemically pure substances, but mixtures of various isomerides; it is very difficult to classify them. Moreover, they are known under a very large number of different fancy names, many of which are applied to products of different composition by different firms. The following is an attempt to classify the various blues.

It has already been shown that a considerable difference exists between pararosaniline hydrochloride or parafuchsine and the ordinary fuchsine of commerce. The former is a uniform compound $C_{19}H_{18}N_3Cl + 4H_2O$, whilst the latter is a mixture of parafuchsine with at least two isomeric homologues. Both these substances may be phenylated; their phenyl- derivatives are blue colouring matters of great intensity and beauty. But a greater difference is found to exist between the phenyl- derivatives of pararosaniline and those of ordinary magenta than even between these two kinds of fuchsine themselves.

The method of phenylation is very remarkable, and quite different from the methods of substituting fatty radicles for hydrogen in the amido- groups of rosaniline. The general method in this case consisted in treating rosaniline base with the halogen derivatives of these radicles. Owing to the great stability of phenyl chloride C_6H_5Cl, the same process cannot be applied for the phenylation of rosaniline. The latter takes place, however, with great facility if we allow aniline to act upon rosaniline, ammonia being given off as a leuco- product:



$$C\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2Cl\end{cases} + 3C_6H_5NH_2 = 3NH_3 + C\begin{cases}C_6H_4.N<^{C_6H_5}_{H}\\C_6H_4.N<^{C_6H_5}_{H}\\C_6H_4.N<^{C_6H_5}_{H}\\\quad Cl\end{cases}$$

Parafuchsine

Triphenyl pararosaniline hydrochloride (rosaniline blue).

This method of phenylation, which has been indicated by Ch. Girard and G. de Laire, is invariably resorted to. It cannot, however, be applied on a practical scale to the hydrochloride, as assumed for simplicity's sake in our equation. The reaction would be much too sluggish. Organic acids must be used in order to get good results. The majority of organic acids has been tried for the purpose; at present, however, only two are used, which give distinctly different results, viz. acetic and benzoic acids. The reason for this difference has not been definitely established, but it is a fact known to every manufacturer that blues of a greenish shade can only be obtained with benzoic acid, whilst acetic acid yields more reddish compounds.

The phenylation of rosaniline cannot be pushed further than to the formation of triphenyl rosaniline. The tetra-, penta-, and hexa- phenyl derivatives are not known. But even the formation of triphenylrosaniline, such as it is indicated by our equation, takes place in three successive stages, one phenyl group entering the molecule after another. It is, however, practically impossible to separate these stages. If, in the beginning of a blue melt, a certain amount of mono-phenylrosaniline be formed, the reaction proceeds simultaneously on this and on rosaniline, which had not yet been attacked; thus, in a second phase, monophenylated, diphenylated rosaniline, and rosaniline (which has not yet been attacked) will be present together. To these the triphenylated compound will presently be added, a very complex mixture being the result. By a very prolonged action it is possible to eliminate rosaniline itself and its monophenylated derivatives completely from the mixture. But some diphenylrosaniline will always remain present. Moreover, all these compounds seem to exist in various isomeric modifications. It is a mixture of these which forms the ordinary *crude* or *opal blue.*

If, instead of pararosaniline, the ordinary rosaniline of commerce be used for the production of the blue (as is the case in most instances) the product becomes even more complicated by the presence of the homologous compounds. Some process of separation must be resorted to, which splits up the crude product into fractions of different shades and reactions; and although some of these are crystallised, it cannot be said with certainty that they represent chemically pure individuals.

Mono- and di- phenyl pararosaniline have hitherto not been prepared in a pure state. Nothing can, therefore, be said of their properties.

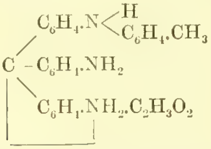
Triphenyl - pararosaniline hydrochloride $C_{37}H_{30}N_3Cl$ is the purest and brightest blue known. It is now invariably prepared by the phenylation of pararosaniline, but it may also be obtained by melting together diphenylamine with oxalic acid. The formic acid evolved in the decomposition of oxalic acid serves to link together three molecules of diphenylamine into one of triphenyl leuco-aniline, which is then slowly oxidised into the rosaniline compound. It was this method which was formerly used for the production of this blue, which therefore is still frequently described as *diphenylamine blue*; it is also called sometimes *methyl blue*, because methyldiphenylamine was sometimes used for its production. Other names for the same product are:

Bleu direct, bleu lumière, bleu de Lyon, bleu de Mulhouse, bleu de nuit, bleu de Paris, light blue, night blue, Paris blue, Bavarian blue.

This product forms a microcrystalline powder of a bronzy appearance, completely insoluble in water, sparingly soluble, with a brilliant blue colouration, in spirit. Its transformation into the soluble diphenylamine blues of commerce will be described hereafter.

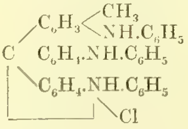
When the same process of phenylation (the particulars of which will be given below) is applied to the ordinary rosaniline of commerce—which is, as will be remembered, a mixture—various products are obtained. Of these the following may be said to have been isolated:—

Monophenyl rosanilines. These are the product of a very moderate phenylation. They are still soluble, in the shape of their acetates, in water, and dye fine purple shades. They have now, owing to the greater cheapness of methyl violets, almost completely disappeared from the market, in which they formerly played an important part under the name of *regina purples* or *regina violets*. It was customary to prepare them, not by the action of pure aniline on magenta acetate, but rather by that of the recovered oils or échappés from the magenta process, which contained a large proportion of orthotoluidine. The action of the latter is slower than that of aniline; it is, therefore, easier to stop the reaction before a considerable proportion of the diphenylated or ditolylated rosaniline is formed. The regina purples consisted, therefore, to a great extent of the ortho-tolylrosaniline, the acetate of which is represented by the following formula:



Diphenylrosanilines. These were invariably obtained, together with the regina purples, from which they are distinguished by their complete insolubility in water. They are, however, still of a purple shade; they are invariably present to some extent in crude tri-phenylrosaniline blue, if the latter be prepared with acetic instead of benzoic acid. This is the reason why such blue is always of a redder shade than the blue prepared with benzoic acid, in which the proportion of diphenylated derivatives is reduced to a minimum. A product which consists chiefly of diphenylated rosanilines, is known under the name of *spirit purple*, *spirit violet*, or *opal violet*; it has also been sold as *regina spirit purple*. From it the *soluble violets* and *purples*, and *alkaline purples* of commerce are derived by sulphonation.

Triphenylrosanilines. The triphenylated derivatives of ordinary rosaniline may be subdivided into two classes: crystalline and uncrystallisable blues. The former may be extracted from every crude blue melt prepared with benzoic acid. They represent in a state of approximate purity the triphenylated derivative of the higher homologue of pararosaniline, and may therefore be represented by the following formula:



It is to this product, which forms the base of the high-class alkaline and water blues of commerce, that we will reserve the name of *opal blue*, which has, however, been indiscriminately applied to a number of various products. This opal blue forms, in the shape of its pure hydrochloride, a mass of distinct, though very small, glittering crystals of a greenish brass-colour. It is completely insoluble in water and in spirit. If it be treated with alcoholic caustic soda, its free base is obtained in the shape of a tarry substance from which the acetate may be prepared by dissolving it in glacial acetic acid, re-precipitating with water. This acetate is soluble in spirit, and, though sparingly, also in water. It was formerly sold and used under the name of *opal blue* 6 *B for cotton*, *Gentian blue*, *Hessian blue*; also the names of *bleu lumière*, *bleu de nuit* (originally used for the para- derivative), were occasionally applied to it. In Germany it was sold under the name of *Feinblau*, *Spritblau*. The latter expression is applied, however, to all blues soluble in spirit, not only to this acetate. Its use has been much restricted of late, owing to the unwillingness of the dyer to use spirit in the dye-bath.

The second class of triphenylated derivatives of ordinary rosaniline, comprises the uncrystallisable proportions of crude blue melts. They contain a mixture of triphenyl- and diphenylrosanilines in various proportions, quite inseparable by the means which are at our disposal. They are (in the shape of hydrochlorides) insoluble in water, soluble in spirit. Caustic soda transforms them into a mixture of the corresponding bases, which are tarry masses. Their shade varies from a purplish-blue to a distinct clear blue of great strength and purity which, however, always shows a purplish hue if looked at by artificial light. This blue forms the starting-point for the production of innumerable brands and qualities of alkaline and water blues, varying in their shade and in the purity and strength of their colour. They are designated, according to the redness of shade, by the letters R R R, R R, R, B, B B, and B B B, whilst 4 B, 5 B, and 6 B may be said to be reserved for the derivatives of the true opal blue of varying purity. A large number of fancy names, such as *China blue*, *marine blue*, *serge blue*, &c., have been invented for this kind of blues.

Besides these blues a special kind of low-class blue should be mentioned which, under the name of *Blackley blue*, has enjoyed, and still enjoys, much favour, especially for dyeing paper-pulp, but also for the production of cheap woollen materials. This is the sulphonation product of a peculiar kind of phenylated rosaniline, prepared by acting with aniline upon *crude* magenta. It is consequently very impure, but also very cheap. It contains a mixture of the phenylation products of all the substances contained in crude magenta.

Triparatolyl-rosaniline has been prepared by acting with paratoluidine in the presence of benzoic acid upon ordinary rosaniline base. It is a blue of remarkable beauty and brilliancy of shade, which offers, however, great resistance to the process of sulphonation. It has, therefore, only been manufactured and sold in the shape of its hydrochloride, soluble in spirit. It is sold for dyeing cotton under the name of *Grünlichblau* (Höchst) or 6 *B extra opal blue* (English manufacturers). It has much gone out of fashion of late years.

Manufacture of blues. An immense number of prescriptions for blue melts has been published, and a larger number still circulates amongst manufacturers. It would be perfectly useless to reproduce any or either of them. The principles upon which they are based may be thus briefly stated:—

For the production of good blues a good and perfectly pure magenta base is the first requirement. For its preparation crystallised fuchsine only should be employed. If crude magenta or any of the magenta residues (cerise, grenadine, &c.) be used, the base obtained can only be employed for the production of *Blackley blues.* Pure pararosaniline, the base prepared from parafuchsine (*Neu-fuchsin*), should be used for the production of the so-called diphenylamine or methyl-blues (direct blues); whilst crystallised base from ordinary fuchsine forms the starting-point for all the ordinary blues from 4 R to 6 B, as well as for regina purples.

The second condition for the production of good blues is the use of very pure aniline, perfectly free from toluidine. It is in the manufacture of blues that the necessity of operating with pure aniline was first felt. The term *aniline for blue* was, therefore, and is still, applied to perfectly pure aniline, boiling within one degree, and having a specific gravity of 1·0268–1·0270. Such aniline can only be prepared from pure crystallisable benzene.

If these two conditions—pure magenta base and pure aniline—be fulfilled, the shade of the blue obtained is still dependent upon

1. The proportions of base and of aniline in the melt. It may be said that greenish blues may only be obtained if a very large excess of aniline be used, whilst reddish blues are produced in melts rich in magenta base.

2. The time and temperature of the melt. The formation of blue begins below 100°C. It proceeds quickly at a higher temperature; 120–140° may be assumed to be the most favourable temperature. From 140–180° certain impurities (diphenylamine?) are formed, which impair the tendency of crystallisation of the blue. The temperature of high-class blue melts should therefore not be raised above 140°. The time required by a blue melt depends upon the proportion of base to aniline, and, to some extent, the quantities operated upon. The process proceeds quickly in highly-concentrated melts. Melts for high-class blues, which contain a large proportion of aniline, require prolonged heating—twenty hours, and even more, before being finished. As a rule, the progress of the melt is tested by placing a drop of the melt on filter paper moistened with spirit. The gradual change of colour may thus be observed with great accuracy. When the melt is finished, there should be no reddish rim visible in the spot produced on the paper.

3. The nature and proportion of the acid used in the melt. It has already been said that organic acids only should be used, the action of hydrochloric acid being too slow. Acetic and benzoic acids are now used exclusively. The action of acetic acid is quicker than that of benzoic acid, but it seems impossible to transform all the rosaniline into its triphenylated derivative by the use of acetic acid. Benzoic acid acts more slowly, but it continues its action until all the rosaniline is transformed into triphenylated derivative. At the same time, the whole of the melt is, even with benzoic acid, not entirely transformed into crystallisable opal. Moreover, acetic acid produces (by its simultaneous reaction on aniline) some acetanilide, which remains in the blue and is apt to prevent its subsequent crystallisation, whilst no benzanilide is formed by heating aniline with benzoic acid. For all these reasons acetic acid is employed in the production of low-class reddish blues (in concentrated melts), whilst benzoic acid only is used for the production of high-class opals. The greater part of the benzoic acid may be recovered from the melt, whilst the recovery of the acetic acid does not pay.

There is no advantage in using other acids instead of acetic and benzoic acid. As a rule, it may be said that the fatty acids (formic, butyric, valeric acids) act similarly to acetic acid, whilst the aromatic acids (toluylic, phthalic, cinnamic acids) may take the place of the benzoic acid.

Upon these conditions all the prescriptions for blue melts are based. Taking the quantity of magenta base to be operated upon as a unit, the quantity of aniline added varies from four to twenty-five times its weight, the quantity of the organic acid from $\frac{1}{10}$ to $\frac{1}{2}$. The conditions of time and temperature have already been stated.

The apparatus necessary for blue-making is very simple as far as the melt is concerned, enamelled cast-iron pots with a lid and stirrer being always used. In the early times of the manufacture of aniline colours it was believed that blue melts could only be made in glass, and on a very small scale. In the 'Fuchsine' factory at Lyons the blue was therefore manufactured in large numbers of glass flasks heated in a sand-bath. At present it is believed that blue melts are best under control in large quantities; large melting-pots are therefore used as a rule. Whilst the melt is in progress ammonia is given off, which carries a certain amount of aniline away. It is advisable to condense this aniline, and to absorb the ammonia by water or sulphuric acid.

When the melt is finished it must be worked up. This may be done by a variety of different methods. Of these the simplest—which is, as a rule, resorted to in the manufacture of low-class and Blackley blues—consists in basifying the melt with a quantity of caustic soda just sufficient to saturate the acid added to the melt. The excess of the aniline is then driven off with steam and recovered. The blue base remains in the still, and is run out whilst still hot, in a tarry state, together with the water. On cooling, it solidifies into a very brittle mass, which may be powdered, dried, and subjected to the process of sulphonation to be described hereafter.

For the production of high-class blues this simple process cannot be adopted. A separation of the crystallisable opal from the uncrystallisable blue, which invariably accompanies it, must take place, and for this separation the melt requires a special treatment. For this there are two distinct processes, of which one is very complete, though costly, because it requires large quantities of spirit. We may call it the *English process*, because it was worked and carried out chiefly in English factories. The other process, which is now used in most of the German works, is very rapid, and requires but little spirit. On the other hand, it does not give so pure a product; we may call it the *German process*.

The English process is the final outcome of the original French process for working up the blue melts, which consisted in boiling them out with dilute hydrochloric acid. The aniline was dissolved out together with the organic acid present, whilst the blue remained in the shape of its hydrochloride as a fine blue precipitate, which was filtered off and washed. It was then ready for sulphonation. When it was discovered that this blue was a mixture of different colouring matters it became customary to separate these by boiling the crude blue with spirit. This dissolved out the lower-class blues, leaving a better product as a residue. By repeating this process frequently, a residue was obtained at last which was quite insoluble in spirit. This represented the purest opal blue obtainable. It was by this tedious process that the once famous 'Bleu Mavi,' or 'Bleu MAVI' was obtained in France and Switzerland. The improved English process much simplified things, and at the same time gave better yields and a purer colour by producing the opal blue in a crystallised condition, in which it is totally insoluble in spirit. This process consisted in adding to the melt (prepared with benzoic acid and a large excess of aniline), when still hot, a certain quantity of aniline hydrochloride; on cooling, the opal blue, being gradually converted into the hydrochloride, settled out in small glistening crystals, whilst the low-class blue remained dissolved in the aniline. The opal was then filtered off, and washed with spirit until quite pure. If necessary, it could be re-converted into base by a treatment with alcoholic caustic soda. The base, re-dissolved in aniline, could again be converted into hydrochloride by again adding aniline hydrochloride. The opal then came out in very fine crystals, which represented the blue in a state of greatest purity. The aniline liquors obtained from these crystallisations had to be distilled in order to recover the spirit. They were then basified in order to decompose the aniline hydrochloride present, the aniline was driven off by steam, and the remaining low-class blue obtained in the shape of base as described. Owing to the large quantities of spirit used for washing the crystallised opal, and the consequent loss of spirit by evaporation, this elegant process (which may be recommended for laboratory experiments) was costly, and unable to compete with the rapid and cheap German process now to be described.

The German process is based upon the fact that the crystallisable blue opal is insoluble in a very hot solution of aniline hydrochloride, whilst the common non-crystallisable blues are soluble in this liquid. The solution of the aniline salt must, however, be so concentrated (in order to act properly) that it would solidify into a mass of crystals if cooled in the least degree. It is rather fused aniline hydrochloride that is required, and not an actual solution of the salt in water. In order to operate properly with such liquids, closed vessels must be used. The following is the principle upon which the plant in the majority of German works is constructed.

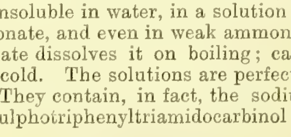
Near the melting-pot a battery of closed iron vessels, lined with lead, is erected. The first of these is filled with a quantity of hydrochloric acid, just sufficient to neutralise the aniline contained in the blue melt. The melt, when finished, is introduced into this vessel by means of air pressure. The vessel is fitted with a stirrer, which stirs up the mixture into a homogeneous mass. This is then pressed into a second vessel, which contains some filtering arrangement, upon which the blue crystals are deposited. The liquid which issues from this vessel is diluted with water, when the common blue hitherto dissolved in it is quickly deposited. The blue crystals remaining on the filter are washed with water, and may be purified by boiling them with spirit.

Blues soluble in water. Very little of the blue that is manufactured is used in the opal state, viz. soluble in spirit. By far the largest proportion of it must be transformed into product soluble in water in order to become a marketable article. For this purpose sulphonation is resorted to.

The sulphonation of triphenylrosaniline takes place very easily, the phenyl radicles attached to the amido- groups being readily substituted by the sulpho- group SO_3H. As there are three of these phenyl radicles present, three sulpho- groups may be introduced into the molecule of the blue. The pure, crystallisable, high-class opal blue is more easily sulphonated than the common blues. The sulphonation takes place in progressive stages, one sulpho- group being introduced after the other. It is difficult to introduce more than two sulpho- groups by the use of ordinary sulphuric acid. Fuming oil of vitriol must be resorted to in order to produce the trisulpho- derivative. As this, however, is hardly ever required, being much too soluble for the purposes of the dyer, common sulphuric acid is invariably used, but the 'extra-strong' quality is as a rule preferred.

If this acid be allowed to act upon an aniline blue, the reaction begins at about 30°C. and results at first in the formation of the monosulpho- derivative. The following are its properties:

In the free state triphenyl rosaniline monosulphonic acid forms blue flakes, which are quite insoluble in water, in a solution of sodium bicarbonate, and even in weak ammonia. Sodic carbonate dissolves it on boiling; caustic soda in the cold. The solutions are perfectly colourless. They contain, in fact, the sodium salt of monosulphotriphenyltriamidocarbinol:



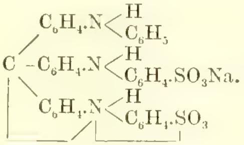
The dry sodium salt is jet black.

This compound has the curious property of combining with wool in an alkaline bath. The wool remains colourless, but after being washed with water it becomes brilliantly blue if immersed in weak sulphuric acid.

This curious property, discovered by Nicholson, has been made use of by wool dyers, who prefer the 'alkaline' or 'Nicholson' blues to all others for the production of bright and brilliant blues.

The alkaline blues originally manufactured by Nicholson and other makers were as nearly as possible the pure sodium salts of the monosulpho- derivative. Owing to the difficulty of dissolving them even in boiling water, another kind of alkaline blues has been produced during the last ten or fifteen years; these new alkaline blues contain a proportion of the disulpho- derivative. They form blue powders, easily soluble in water, giving a solution which is distinctly blue. The use of these new alkaline blues is exactly similar to that of the old quality.

If the sulphonation of the opal blue be carried farther by raising the temperature and allowing the reaction to continue for a longer period, the monosulpho- acid gradually disappears and is replaced by the disulpho- derivative. This is insoluble in weak sulphuric acid, but rather soluble in pure water, with an intensely blue colouration. Its sodium salt forms bright coppery masses soluble in water with a blue colouration. This salt contains probably the compound represented by the following formula:



The disulpho- derivatives of the various classes of triphenyl-rosanilines are known under the names of *cotton blue*, *water blue*, *china blue*, *navy blue*, *Guernsey blue*, and many others, which are again sub-divided by the use of the letters R and B. Thus a 6B cotton blue is the disulpho-acid of a very high-class, crystallisable opal blue, whilst a 4R Guernsey or navy blue would be a reddish-tinted blue, manufactured from an opal prepared with acetic acid and a small excess of aniline in the melt.

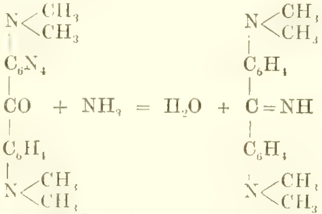
The practical process of sulphonation, though very simple, requires great care and attention on the part of the manufacturer. The sulphonation is carried on in cast-iron pots into which the necessary quantity of sulphuric acid is introduced. The opal blue, which should be finely powdered and perfectly dry, is then stirred in, and the temperature should be raised gradually. Samples should be drawn from time to time, and the precipitate produced by the addition of water must be examined as to its solubility in water, weak ammonia, sodic carbonate, and caustic soda. When the desired degree of solubility is obtained, the liquid is poured into water, and the blues filtered off and carefully washed. When quite free from acid, they are dissolved in the quantity of caustic soda necessary; the solution is then filtered, and evaporated to dryness in jacketed pans. Cotton blues should be freed from the excess of sulphuric acid by the addition of slaked lime. The solution of the calcium salt is filtered and converted into the sodium salt by double decomposition with sodic carbonate. After another filtration, the solution of the blue is evaporated to dryness. Certain artifices are required to produce porous masses, such as the brand known as *china blue*, which is manufactured for export, and required to possess a given bulk for a given weight.

On the whole, the manufacture of aniline blues, though simple in its principles, may be said to be one of extreme difficulty, requiring more care, attention, and skill than almost any other branch of the industry of artificial colouring matters.

Appendix to basic triphenylmethane colouring matters.

Auramine. This dye-stuff, though a derivative of diphenylmethane, is so closely connected with the manufacture of crystallisable violet, that it cannot be omitted from this sketch.

It has been shown that crystal violet, as well as Victoria blue and other dye-stuffs, are manufactured from dimethyl and diethyl diamidobenzophenone. Now, if these ketones be heated with ammonium chloride in the presence of zinc chloride, an interesting reaction takes place at the temperature of 150-160°C. The oxygen of the ketone is replaced by the imido-group NH, thus:



$$\begin{array}{ccccccc} N{<}^{CH_3}_{CH_3} & & & & & & N{<}^{CH_3}_{CH_3} \\ | & & & & & & | \\ C_6N_4 & & & & & & C_6H_4 \\ | & & & & & & | \\ CO & + & NH_3 & = & H_2O & + & C{=}NH \\ | & & & & & & | \\ C_6H_4 & & & & & & C_6H_4 \\ | & & & & & & | \\ N{<}^{CH_3}_{CH_3} & & & & & & N{<}^{CH_3}_{CH_3} \end{array}$$

The ketimides thus obtained are yellow colouring matters, and have received the name of *auramines*. The auramine of commerce is the monohydrochloride of tetramethyl diamidobenzoketimide, containing one molecule of water of crystallisation:

$$C_{17}H_{21}N_3.HCl + H_2O.$$

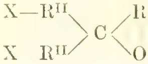
It forms a yellow powder easily soluble in water. It is exclusively used for dyeing and printing on cotton.

Substituted auramines may be obtained by using the hydrochlorides of primary bases instead of sal-ammoniac. Thus a phenylated auramine of orange colour may be produced by acting with aniline hydrochloride upon tetramethyl diamidobenzophenone.

The auramines were discovered by Caro and Kern in 1884. They form the subject of the Eng. Pats. 5512, 1884, and 5741, 1884, and the Germ. Pats. No. 29060 and 31936.

II. The Aurine Group.

The characteristic difference of this group from the preceding one has already been discussed. It is sufficient to reproduce the typical formula given for the members of this group:

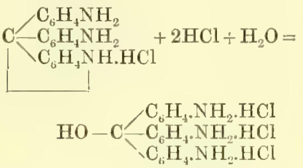


$$\begin{matrix} X{-}R^{II} \\ X\ \ R^{II} \end{matrix} {>} C {<} \begin{matrix} R^{II} \\ O \end{matrix}$$

from which it will be seen that they invariably contain oxygen.

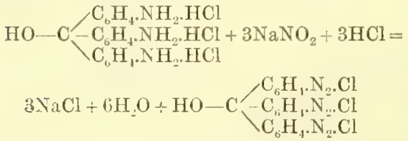
The generic relation between the fuchsine and the aurine groups will be best seen by showing how the typical representative of the former, parafuchsine, may be transformed into the first representative of the aurine group, aurine itself.

We know that parafuchsine, if treated with an excess of acid, is transformed into the triacid salt of triamidotriphenylcarbinol:



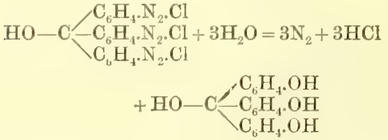
$$C\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH.HCl\end{cases} + 2HCl + H_2O = HO-C\begin{cases}C_6H_4.NH_2.HCl\\C_6H_4.NH_2.HCl\\C_6H_4.NH_2.HCl\end{cases}$$

Now this salt, if treated with nitrous acid, is transformed into the corresponding diazo-compound



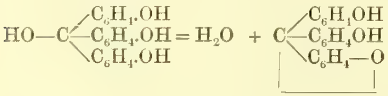
$$HO-C\begin{cases}C_6H_4.NH_2.HCl\\C_6H_4.NH_2.HCl\\C_6H_4.NH_2.HCl\end{cases} + 3NaNO_2 + 3HCl = 3NaCl + 6H_2O + HO-C\begin{cases}C_6H_4.N_2.Cl\\C_6H_4.N_2.Cl\\C_6H_4.N_2.Cl\end{cases}$$

This, on being boiled with water, loses nitrogen and is transformed into trioxy-triphenylcarbinol



$$HO-C\begin{cases}C_6H_4.N_2.Cl\\C_6H_4.N_2.Cl\\C_6H_4.N_2.Cl\end{cases} + 3H_2O = 3N_2 + 3HCl + HO-C\begin{cases}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.OH\end{cases}$$

The latter loses, in *statu nascendi*, one molecule of water, being transformed into its inner anhydride, aurine:



$$HO-C\begin{cases}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.OH\end{cases} = H_2O + C\begin{cases}C_6H_4OH\\C_6H_4OH\\C_6H_4-O\end{cases}$$

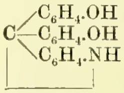
Thus aurine is parafuchsine in which all nitrogen has been replaced by oxygen.

This mode of formation has long been known, not for aurine itself, but for its higher homologue, rosolic acid, which was prepared from the ordinary fuchsine or magenta by the process described. The many co-ordinate points of aurine and rosolic acid have been recognised at an early period. On the other hand, chemists were aware of the distinct difference between aurine and rosolic acid, which is just as considerable as that existing between parafuchsine and its higher homologue.

When an insight into the nature of the fuchsine group had been obtained, the knowledge of the constitution of the aurine group followed as a natural consequence.

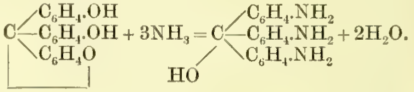
But even before this was the case, another connection was discovered between aurine and fuchsine.

It had long been known that aurine (the mode of formation of which will be given later on) may be modified by heating it with alcoholic ammonia. F. Persoz produced a red dye-stuff, which he called *pæonine*, by this process. This was, in all probability, aurine imide:



$$C\begin{cases}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.NH\end{cases}$$

In 1878, Dale and Schorlemmer, whose researches on aurine are of great importance, showed that aurine, by very prolonged heating with alcoholic ammonia, may be transformed into pararosaniline

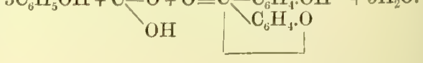


$$C\begin{cases}C_6H_4.OH\\C_6H_4.OH\\C_6H_4O\end{cases} + 3NH_3 = \underset{HO}{C}\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{cases} + 2H_2O.$$

Thus the connection of the two typical dye-stuffs was definitely established. At present we know that the aurine group contains the acid counterparts to the basic members of the fuchsine group. An immense number of them is known and described in chemical literature. As, however, almost all of them are of no practical value whatever, it would be useless to enumerate them in this article. We will therefore describe only those substances of the aurine group which are of some practical interest. There are very few of them.

1. *Aurine* $C_{19}H_{14}O_3$. The discovery of this substance, or one very nearly related to it, dates as far back as 1834, when F. Runge, the pioneer of the chemistry of coal-tar, observed that crude carbolic acid (containing cresol) was transformed into an acid red dye-stuff by oxidation. Later on (1859), Kolbe and Schmitt and T. Persoz simultaneously observed that pure phenol, when heated with oxalic acid, or with oxalic acid and sulphuric acid, was transformed into a similar red substance. The manufacture of the new dye-stuff was first taken up in Lyons by the firm Guinon and Marnas. Later on, it was carried out on a large scale by C. Calvert and by C. Lowe; also by Roberts, Dale, & Co., in Manchester. The crude aurine thus obtained is a non-crystallisable, brittle, pitchy mass, of a brilliant green metallic aspect, insoluble in water, but soluble in caustic soda solution, with a magnificent red colouration. It dyes silk and wool from an acid bath, producing an orange shade on these fibres. It was much used on silk in former days, but its use has been abandoned since the introduction of the azo- colouring matters, which produce brighter and faster shades.

The researches of Dale and Schorlemmer, Zulkowski, and others have shown that common aurine consists of a mixture of a number of substances which, in a pure state, are well crystallised. Of these, aurine itself $C_{19}H_{14}O_3$, oxyaurine $C_{19}H_{16}O_6$, methylaurine $C_{20}H_{16}O_3$, and pseudo-rosolic acid $C_{20}H_{16}O_4$, may here be mentioned. All these substances are produced by the action of nascent formic acid (generated from the oxalic acid) upon phenol. This mode of formation of aurine itself may be represented by the following equation:

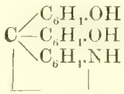


$$3C_6H_5OH + C\begin{cases}H\\=O\\OH\end{cases} + O = C\begin{cases}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.O\end{cases} + 3H_2O.$$

A large number of other reactions have been observed in which aurine is formed to a greater or lesser extent. Thus, for instance, it is obtained by acting with formic aldehyde, with iodoform, with chloroform, and caustic potash on phenol. These reactions have never attracted the attention of manufacturers, aurine having lost its practical interest.

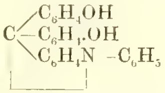
The sodium salt of crude aurine is known in commerce under the name of *yellow coralline.*

2. *Pæonine, coralline red, aurine red* is the sodium salt of the reaction product of alcoholic ammonia upon aurine, which has already been mentioned, and which is, in our opinion, aurine imide:



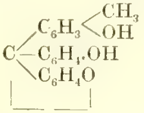
$$C\left\langle\begin{matrix}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.NH\end{matrix}\right.$$

3. *Azuline* is a similar product, of a dirty violet shade, obtained by heating aurine with aniline. It is probably phenylated aurine imide:



$$C\left\langle\begin{matrix}C_6H_4OH\\C_6H_4.OH\\C_6H_4N-C_6H_5\end{matrix}\right.$$

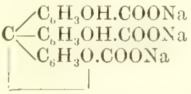
4. *Rosolic acid* is the name which was originally given by Runge to the oxidation product of crude carbolic acid. For a long time it was considered synonymous with aurine. At present it is reserved for the product obtained from the ordinary fuchsine of commerce by the diazotising process. It forms magnificent blue needles, which, being homologous to true aurine, have the composition $C_{20}H_{16}O_3$:



$$C\left\langle\begin{matrix}C_6H_3\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.\\C_6H_4.OH\\C_6H_4O\end{matrix}\right.$$

It dyes silk and wool orange shades, similar to those obtained with aurine. It is of no practical interest.

5. *Chrome violet* $C_{22}H_{13}O_9Na_3$ is the only member of the aurine group which is of considerable practical value. It is the sodium salt of aurine-tricarbonic acid:

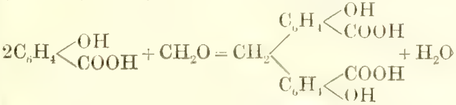


$$C\left\langle\begin{matrix}C_6H_3OH.COONa\\C_6H_3OH.COONa\\C_6H_3O.COONa\end{matrix}\right.$$

It was discovered in 1889 by Sandmeyer, and patented (Germ. Pat. 49970, J. R. Geigy). It is prepared by acting with formic aldehyde, or with a mixture of methylic alcohol and sodic nitrite, upon a solution of salicylic acid in sulphuric acid. The carboxyl groups are in ortho- position to the hydroxyl groups. The result of this arrangement is that the dye-stuff combines readily with metallic mordants of the iron group, and especially with chrome mordant, producing violet shades of considerable fastness on cotton. It is chiefly used for printing on cotton.

The process patented for the production of chrome violet is interesting, because it forms a general and excellent synthetical method for the production of aurines. It is strictly analogous to the new synthetical method adopted for the production of 'Neu-fuchsin' by the 'Farbwerke' of Höchst. Two stages may be distinguished in the process:

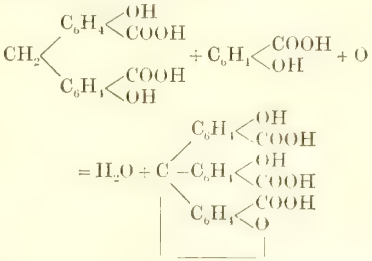
(*a*) In the first stage, formic aldehyde (or methylal) acts upon two molecules of the phenol—in the case of chrome violet, salicylic acid—forming the diphenylmethane derivative (methenyl salicylic acid):



$$2C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right. + CH_2O = CH_2\left\langle\begin{matrix}C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.\\C_6H_4\left\langle\begin{matrix}COOH\\OH\end{matrix}\right.\end{matrix}\right. + H_2O$$

This reaction may be facilitated by the addition of condensing agents, such as hydrochloric acid and others.

(*b*) In the second stage, the diphenylmethane derivative is simultaneously condensed and oxidised with another molecule of the phenol into the corresponding aurine by the mixture of sulphuric acid and sodic nitrite:



$$CH_2\left\langle\begin{matrix}C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.\\C_6H_4\left\langle\begin{matrix}COOH\\OH\end{matrix}\right.\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}COOH\\OH\end{matrix}\right. + O$$

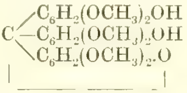
$$= H_2O + C\left\langle\begin{matrix}C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.\\C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.\\C_6H_4\left\langle\begin{matrix}COOH\\O\end{matrix}\right.\end{matrix}\right.$$

Any phenol, or substitution product of a phenol, may be substituted for the salicylic acid in this process.

Quite recently, N. Caro (B. 25, 940) prepared a large number of carboxylated aurines by this process, substituting resorcylic, gallic, and cresotinic acid for the salicylic acid in the patented process. The compounds obtained proved to be very similar to chrome violet.

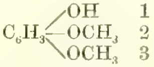
6. Of the large number of aurines prepared, only one more need be mentioned in this sketch: *pittakal*, a curious substance discovered in 1835 by Reichenbach in certain portions of beech-wood tar. Liebermann more closely investigated this substance, and gave to it the name of *eupittonic acid* (B. 1876, 9, 334; 1878, 11, 1104). Hofmann determined its constitution (B. 1878, 11, 1455; 1879, 12, 1371, 2261).

Pittakal is hexamethoxyl aurine:



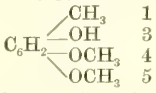
$$C\left\langle\begin{matrix}C_6H_2(OCH_3)_2OH\\C_6H_2(OCH_3)_2OH\\C_6H_2(OCH_3)_2O\end{matrix}\right.$$

formed by the simultaneous oxidation of dimethylpyrogallol:



$$C_6H_3\left\langle\begin{matrix}OH & 1\\OCH_3 & 2\\OCH_3 & 3\end{matrix}\right.$$

and dimethyl methylpyrogallol:



$$C_6H_2\left\langle\begin{matrix}CH_3 & 1\\OH & 3\\OCH_3 & 4\\OCH_3 & 5\end{matrix}\right.$$

which are both contained in wood tar. The methyl group of the second compound yields the central carbon atom, the same as cresol did in the formation of the rosolic acid observed by Runge.

Pittakal is an orange substance, crystallising in beautiful crystals when pure. Its solution in caustic alkalis is of a beautiful blue colour.

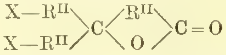
By heating pittakal with ammonia, Grätzel obtained a violet colouring matter, which proved of no practical value.

III. The Phthaleine Group.

The phthaleines were discovered by Baeyer in his memorable researches on the condensation of phthalic acid with aromatic hydrocarbons and phenols. Their constitution was, however, at first misunderstood. In 1880, when the curious properties of phthalic anhydride became more definitely known, the error was corrected and the phthaleins were recognised as congeners of the triphenylmethane group.

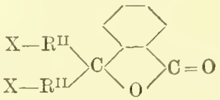
It is a well-known fact that every orthodicarbonic acid is capable of forming, by losing the elements of water, an inner anhydride. These anhydrides act very easily on phenols, in some cases without the addition of condensing agents. Water is again eliminated, and a dye-stuff formed in every instance. Of the many colouring matters thus obtained, those prepared from phthalic anhydride only have, with one exception, become of general and practical interest, and these will here be described.

It has already been shown that the typical formula of the phthaleines is



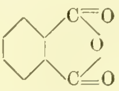
in which X stands for a salt-forming group, which may be either OH or NH_2, or NH_2 substituted by organic radicles.

The central carbon is yielded by one of the carbonyl groups of the anhydride of an orthodicarbonic acid. If we restrict our consideration to phthalic anhydride, the formula may thus be modified:

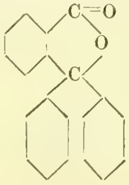


phthalic acid being phenylene-orthodicarbonic acid.

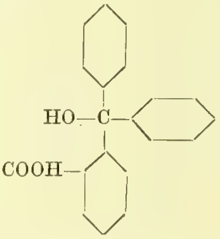
Phthalic anhydride, though perfectly symmetrical in its constitution



acts, in condensations, like an asymetrical compound, only one of the carbonyl groups being attacked and losing its oxygen. Thus, by being condensed with two molecules of benzene it yields diphenyl phthalide or phthalophenone:



which is the parent substance of all the phthaleins, just as triphenylmethane is the parent substance of the fuchsine and aurine groups. Diphenyl phthalide, however, is but the inner anhydride of triphenylcarbinolorthocarbonic acid:

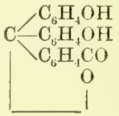


hence the near relation between the phthaleine, fuchsine, and aurine groups.

It will be seen that in diphenylphthalide the link between the central carbon and one of the phenyl groups, which we have shown to be necessary for the formation of dye-stuffs, exists already, whilst in triphenylmethane it does not exist. Thus diphenylphthalide is a fine chromogen, requiring only the entrance of salt-forming groups in order to give rise to colouring matters. The simplest coloured derivatives of diphenylphthalide are diamidophthalophenone and dioxyphthalophenone. The former of these has been obtained by Baeyer in reducing the dinitroderivative of diphenylphthalide. It is (like rosaniline) faintly coloured in the free state, but it dissolves, with a bright violet shade, in weak acids.

Dioxyphthalophenone is generally known to chemists under the name of phenolphthalein.

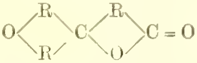
1. *Phenolphthalein* $C_{20}H_{14}O_4$ was discovered by Baeyer in 1871 (B. 1871, 4, 658). Its constitution is



It is easily prepared by heating phthalic anhydride with phenol in the presence of sulphuric acid or stannic chloride. It forms pale-yellow crystals, which dissolve with a fine red colour in caustic alkalis. Its only use is that of an indicator for alkalimetric purposes.

2. *Tetranitrophenolphthalein* $C_{20}H_{10}N_4O_{12}$ has been proposed as an orange colouring matter for wool. Its sodium salt $C_{20}H_8N_4O_{12}Na_2$ is sold as an orange powder under the name of aurotine. It was discovered by C. Dreyfus, H. Bull, and T. Hall, and patented in England under No. 3441 (1889), in Germany under the No. 52211. In a pure state free tetranitrophenolphthalein forms orange crystals, melting at 344°.

It has long been known that phenolphthalein is not a good dye. The same applies to all the ordinary typical phthaleins. Phthalophenone (diphenylphthalide) is but a poor chromogen, but its properties are at once improved (as has already been shown above) if the two phenyl-radicles in its molecule be linked together by another group, preferably oxygen. We thus come to another chromogen:



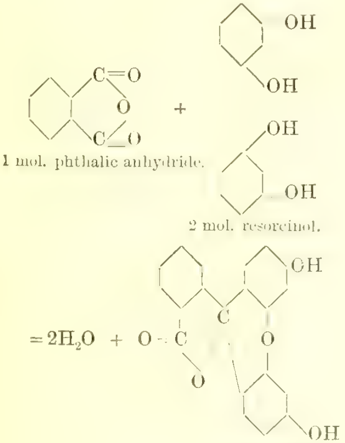
which by the introduction of salt-forming groups gives rise to some of the most beautiful dye-stuffs ever discovered. As in all cases, the salt-forming groups introduced may be either the OH, hydroxyl or the NH_2 amido-group; and in the latter hydrogen may be replaced by organic radicles. We thus get phthalein colouring matters of either phenolic (acid) or amidic (basic) character. For a long time the former alone were known; we will, therefore, consider them first.

A. *Acid phthalein dye-stuffs.*

The prototype of these is—

1. *Fluorescein* $C_{20}H_{12}O_5$. This beautiful substance is formed most easily if phthalic anhydride and resorcin be mixed in molecular proportions and heated to 190°. In the factories this operation is carried out in enamelled cast-iron pots, heated in an oil bath. The ingredients melt, and large quantities of steam are given off. When the reaction is finished the mass solidifies into a cake of dark-brown colour, which consists of almost pure fluoresceine.

In this reaction two molecules of resorcin combine with one of phthalic anhydride. At the same time they interact upon one another, losing one molecule of water, and forming an anhydride:



Fluoresceine.

Pure fluorescein is a brick-red crystalline powder, quite insoluble in water, sparingly so in the majority of other solvents. In caustic alkalis and in ammonia it dissolves with a brown colour. The solutions have, especially when dilute, a most brilliant and beautiful green fluorescence. Hence the name of the substance.

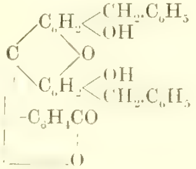
The crude fluorescein obtained in the manufacture, as above described, seems to contain two modifications of the substance (which may be isomerides). By treating the crude cake with boiling spirit, a certain amount of a soluble, non-crystallisable fluorescein is extracted, whilst the greater proportion of it remains undissolved, and is obtained as a crystalline residue on filtering. This process of purification is invariably used in the manufacture of the dye-stuff. Both the soluble and the insoluble part are worked up in the manner to be described hereafter, the insoluble fluorescein giving the better and purer qualities of the dye-stuffs, whilst the low-class qualities are made from the soluble fluorescein obtained by evaporating the alcoholic extract.

A small quantity of the fluorescein manufactured is transformed into its sodium salt

$$C_{20}H_{10}O_5Na_2,$$

which is sold, under the name *uranine*, in the shape of a yellow powder, very soluble in water. It is used for dyeing pale yellows on silk.

If benzylic chloride and some sulphuric acid be added to the fluorescein melt a substance is obtained which is supposed to be benzyl-fluorescein:



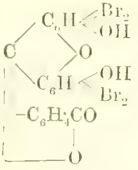
Its sodium salt is sold as a yellow dye-stuff under the name *chrysolin*. This substance, discovered by Reverdin in 1877, is not of much practical importance.

By far the greater part of the fluorescein produced is transformed into very beautiful red colouring matters by the introduction of halogen atoms into its molecule. The dye-stuffs so prepared are known by the generic name of *eosines*.

If fluorescein be treated by substituting reagents, it is generally observed that four atoms of hydrogen are replaced by other groups. Further investigations have shown that this substitution takes place in the phenyl radicles, which entered the fluorescein in the shape of resorcinol, whilst the phenyl radicle derived from the phthalic anhydride is never attacked by these reagents.

The most important of the dye-stuffs so prepared is

2. *Eosin* $C_{20}H_6O_5Br_4K_2$, the potassium salt of tetrabromofluorescein. The sodium salt is also occasionally met with, but it does not crystallise so well. The constitutional formula of eosin is:



Eosin is prepared by acting with four molecules of bromine (Br_2) upon one molecule of fluorescein. The crystallisable modification of the latter is used for the production of a good product. On the small scale a solution of the fluorescein in glacial acetic acid is prepared, and the bromine introduced gradually.

For manufacturing purposes glacial acetic acid is too expensive. The following process may be used instead, which admits of operating in aqueous solutions.

The bromine is dissolved in exactly the necessary quantity of caustic soda, and the solution is evaporated to dryness. The resulting salt consists of a mixture of sodium bromide and sodic bromate. It is dissolved in water and mixed with a solution of the theoretical quantity of fluorescein in caustic soda. The mixture is then acidified with hydrochloric acid. The bromine generated acts at once upon the fluorescein, and the precipitate obtained is eosin, which need only be dissolved in a solution of potassium carbonate and evaporated to crystallisation.

The quantity of bromine used may be reduced to half (two molecules or four atoms) by using a mixture of potassic bromide and potassic or sodic chlorate, instead of the salt obtained by evaporating the solution of bromine in caustic soda.

This process, though cheap and simple, is not generally used, because the bromine is found to act too energetically. A certain amount of the eosin is destroyed, and the remainder is not so brilliant in colour as it might be.

The bromination proceeds much better in an alcoholic solution; alcohol is, therefore, frequently used for the purpose in the manufacture of eosin. The fluorescein is finely ground, and suspended in strong spirit. The necessary quantity of bromine is added. The bromination takes place slowly and gradually, and an excellent product is obtained. The spirit is recovered by distillation.

In order to reduce the bromine in this as in the aqueous process to two instead of four molecules, the addition of a chlorate is necessary. But a chlorate must be used which is soluble in spirit. Cupric chlorate is preferred to any other. It is prepared by mixing concentrated aqueous solution of sodic chlorate and cupric chloride or sulphate. The solution obtained is added to the operation in progress.

Eosin forms either a dark-brown powder, or dark-brown crystals with a green metallic lustre. The potassium salt may also be obtained in flesh-coloured crystals by re-crystallisation from spirit. These crystals contain alcohol of crystallisation. According to strength and purity of shade, the commercial eosines are distinguished by certain letters and additions, such as 'eosin B,' 'A,' 'GGF,' 'DH,' 'extra,' 'extrafine,' 'soluble,' and others. All these brands dissolve easily in water, with a scarlet colouration. Dilute solutions show a marked greenish fluorescence.

Eosin is used for dyeing silk and other fibres, also for staining paper, and for preparing red inks of a very fine scarlet colour. Large quantities are used for the latter purpose. Eosine is not a fast colour, but its brilliancy of shade secures a ready sale for the large quantities produced.

3. **Eosin soluble in spirit** or **erythrin** (*Primrose, methyl-eosin*). These names are applied to certain products, which are produced by boiling eosine, dissolved in spirit, with caustic soda and methylic iodide, or ethylic bromide. One of the hydroxyl groups is thus alkylated. The sodium salts thus obtained form glistening crystals, insoluble in water but soluble in spirit. Small quantities of this substance are prepared and used as an addition to the vermilion used in cotton printing, in order to increase the brilliancy of its shade. Spirit eosin was formerly also used for silk dyeing, but for this purpose it has been replaced by the bluish eosines soluble in water, to be described later on.

If both the hydroxyl groups of eosin are to be alkylated, this can only be effected by acting with alkylic iodide or bromide upon the silver salt of eosine. The dialkyl-ethers thus obtained are colourless.

4. **Eosin scarlet** (*Eosin B, BN, BW, scarlet, J, JJ, V, &c.*). Sodium salt of dinitrodibromofluoresceine $C_{20}H_6N_2O_9Br_2Na_2$.

If fluorescein be treated with nitric acid, dinitrofluorescein is obtained, which has found no application as a colouring matter. But by subsequent bromination it yields a brilliant scarlet. The same product (or an isomeride very similar to it) may be prepared by first brominating the fluorescein and then treating it with nitric acid.

This dye-stuff was hailed with enthusiasm when it made its appearance in 1875, but its use was soon much restricted by the introduction of the scarlet azo- dyes, which are quite as brilliant, but at the same time faster, cheaper, and more easy in their application.

5. **Erythrosin** (*Bluish Eosin, Dianthin, Primrose soluble, Pyrosin B*, and other names).

This is the sodium salt of tetraiodofluorescein $C_{20}H_6O_5I_4Na_2$. The potassium salt is also met with occasionally. It is prepared by iodising fluorescein with iodine and oxidising agents, such as mercuric oxide, iodic acid, cupric chloride, &c. It may also be prepared by introducing iodo-chlorine into an alcoholic suspension of fluoresceine.

Erythrosin dissolves in water, with a fine red colour, and very slight fluorescence. It dyes silk in shades which are much bluer than those obtained with eosine.

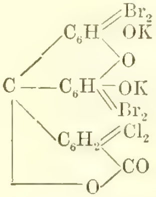
Erythrosin was introduced into the market in 1876 by Bindschedler and Busch. It was well received by the silk dyers. Owing to the high price of iodine, a mixture of eosine and Bengal red is now used for producing the same shades.

There is one application, however, for which pure erythrosine is still used—for producing orthochromatic dry plates for photographic purposes. As a sensitiser of silver bromide, erythrosin holds the first place of all colouring matters tried hitherto.

Di-iodofluorescein was sold and used for a very short time as an orange dye-stuff, under the name 'pyrosine J.'

6. **Phloxin** (*Potassium salt of dichloro- or tetrachloro- tetrabromofluoresceine*).

This colouring matter, discovered in 1876 by Nölting, together with the following ones, formed a new departure in the manufacture of the eosin dyes. The characteristic feature of these substances is the fact that they contain halogen atoms, substituted for hydrogen, not only in the resorcinol groups, but also in the phenyl group derived from the phthalic anhydride. Now, it has already been said that a substitution of this kind cannot be effected in ready-made fluoresceine. To prepare phloxin, therefore, or any of its congeners, a special fluorescein must be used, prepared not with ordinary phthalic anhydride, but with the anhydrides of dichloro- or tetrachloro- phthalic acid. Both of these give colouring matters of very similar shades, the tetrachloro- derivatives being but very little bluer than the dichloro- derivative. The process of manufacture is identical with that described for eosin. The constitutional formula of phloxine is:



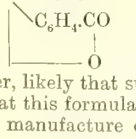
Commercial phloxine is a red powder, soluble in water, with a red colour and no fluorescence. It dyes beautiful bluish-red shades on silk, which resemble those obtained with erythrosine.

7. **Cyanosin** is the monomethylic ether of phloxin. It is soluble in spirit, and dyes shades still bluer than phloxin.

8. **Bengal red** (*Rose Bengale N*) $C_{20}H_4Cl_2I_4O_5K_2$ is the iodo- derivative of this series. It is the bluest eosin dye-stuff obtained. It is very expensive, and was formerly used in large quantities to produce the most brilliant bluish-reds on silk. It has now, to a great extent, been replaced by the rhodamines. Its methylic ether, soluble in spirit, received the name of cyanosin B. Its application never became important.

The phthalein derivatives of resorcinol are all very brilliant dyes. There are, however, some other acid phthaleines which, though important as colouring matters, are of much more sober hues. They are derivatives of pyrogallol.

9. **Gallein** $C_{20}H_{10}O_7$. If phthalic anhydride be condensed with pyrogallol, the reaction takes place quite as easily as with resorcinol. But the product obtained is not, as might be expected, a dioxyfluoresceine. Not only two hydroxyl groups interact upon each other, as was the case with fluoresceine, but four of them. Thus the two phenolic radicles are linked together by two oxygen atoms. The constitutional formula generally adopted for gallein is



It is, however, likely that subsequent researches will show that this formula must be modified.

For the manufacture of gallein it is not necessary to prepare pure pyrogallol. Gallic acid may be used instead, which, losing carbonic anhydride, is at once transformed into gallein by the action of the phthalic anhydride.

Gallein is generally sold in the shape of a violet paste. It is sparingly soluble in water, easily soluble in caustic alkalis, with a bright-blue colouration. It dyes mordanted wool and cotton. Chrome mordants are used preferably, and dark-violet shades are obtained.

On account of the similarity of the application of gallein to that of alizarin, gallein is also sold under the name of *alizarin violet* or *anthracene purple.*

10. **Cœrulein** (*Alizarine green, anthracene green*) $C_{20}H_8O_6$. This is one of the most important dye-stuffs for wool and cotton, dyeing a beautiful and very fast olive green on chrome mordants. The cotton printer uses it constantly, both pure and mixed, with other dye-stuffs of the alizarine family.

It was discovered in 1871 by A. Baeyer, who obtained it by heating gallein with concentrated sulphuric acid to 200°. By the same process it is now prepared in immense quantities on the large scale.

Cœrulein forms a black paste, insoluble in water. It is soluble in caustic alkalis, with a greenish-blue colouration.

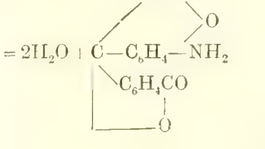
The constitution of cœrulein is not known. The attempts which have been made to elucidate it cannot claim to have produced conclusive evidence.

11. **Cœrulein S** (*soluble cœrulein*) $C_{20}H_{10}O_{12}S_2Na_2$. This is the product of the reaction of sodic bisulphite upon cœrulein; its manufacture is carried on by the Badische Aniline and Soda works of Ludwigshafen. It forms a black powder, soluble in water, with a brown colouration. It is easily decomposed by the addition of acids or by heat. It is used for the same purposes as cœrulein, and is very convenient, on account of its easy solubility. In dyeing with it, it is, of course, decomposed, the ordinary cœrulein being deposited on the fibre.

B. *Basic phthalein dye-stuffs.*

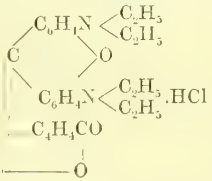
For a long time these were not known. The manner in which they may be obtained had, of course, suggested itself to the consideration of chemists, but the substances required for their synthesis seemed to be quite out of the reach of the manufacturer. In 1887, however, M. Ceresole, of the Badische Anilin- und Soda-Fabrik, successfully effected the synthesis of the first basic phthalein, which proved to be of such value that a thorough search for a good means of preparing the necessary ingredients was made, which led to complete success.

To obtain the basic substance analogous to fluoresceine, it is merely necessary to replace one of the hydroxyl groups of resorcinol by an amido- group; or, in other words, to employ metamidophenol instead of resorcinol:



Experience has, however, shown that the compound thus obtained has no practical value. If, however, diethylmetamidophenol is used instead of the metamidophenol, a most beautiful colouring matter is obtained, known under the name

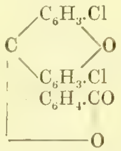
1. **Rhodamin B** $C_{28}H_{31}N_2O_3Cl$. The commercial product is the monohydrochloride:



It forms beautiful needles of a metallic green appearance, easily soluble in both water and spirit. Weak solutions show a most magnificent orange fluorescence, which disappears on heating, and reappears in the cold. This is the most beautiful red colouring matter ever prepared, dyeing silk, wool, and cotton a most brilliant pink of a bluish shade.

The process described for the production of rhodamine is patented by the Badische Anilin- und Soda-Fabrik, Eng. Pat. No. 15374, 1887; Germ. Pat. No. 44002. The diethylmetamidophenol is prepared from diethylanilin by heating it with fuming sulphuric acid to 60°C., diethylanilin metasulphonic acid is formed, which yields the phenol by fusion with caustic soda.

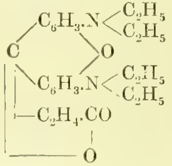
There is, however, another process for the manufacture of rhodamine, discovered by the Farbwerke of Höchst (Germ. Pat. No. 48367, 1888). It consists in treating fluorescein with phosphorous pentachloride, when the fluorescein chloride



is formed. This is transformed into rhodamine if heated with diethylamine under pressure. Rhodamine has remained, hitherto, the only basic phthalein of practical interest.

2. **Rhodamine S** $C_{20}H_{23}N_2O_3Cl$ and $C_{24}H_{31}N_2O_3Cl$.

These two colouring matters, which are identical in their practical properties and applications, are not, strictly speaking, triphenylmethane derivatives; nor are they derived from phthalic acid. They must, however, be mentioned here, because they are near congeners of rhodamine B. They are obtained by treating dimethyl- or diethyl- metamidophenol, not with phthalic, but with succinic, anhydride. Succinic acid is the typical orthodicarbonic acid of the fatty series. Like phthalic acid, it forms an anhydride, which condenses with resorcinol into fluorescein-like dye-stuffs; these, however, offer no practical interest. The succineines of dimethyl- and diethyl- metamidophenol, however, show a sufficient difference from rhodamine to be manufactured and sold as a special brand. The constitution of the diethyl compound may be represented by the following formula:



It is, therefore, not a triphenylmethane derivative, but one of ethyldiphenylmethane.

Rhodamine S shows great affinity to unmordanted cotton. It is one of the few members of the triphenylmethane group which may be considered as what is now called a substantive colouring matter.

The properties of rhodamine S are very similar to those of rhodamine B. It forms crystals with a green metallic lustre, easily soluble in water, with a red colouration, and a marked yellow fluorescence. The shades obtained with it are yellower than those produced with rhodamine B.

The above sketch only includes such triphenylmethane derivatives as have proved to be of practical value. Both their number and properties are sufficient to show that the triphenylmethane group is of the greatest importance for the chemistry of dye-stuffs, and it is probable that its importance may be still increased by future additions. O. N. W.

TRIPHYLLINE *v.* Lithium.

TRIPOLI. A mineral, used for polishing, consisting mainly of silica associated with small quantities of alumina and ferric oxide, occurring massive in beds and in nodules. Colour varying from white or yellow to grey or black, is soft and friable, and of sp.gr. 1·86 to 2·7. Seems to consist mainly of the skeletons of Infusoria. Tripoli is found in France, Saxony, Bohemia, Tuscany, Tripoli, Corfu, &c.

TROGERITE *v.* Uranium.

TROILITE. A name applied by Haidinger to ferrous sulphide FeS, occurring in meteorites.

TRONA. Native sodium sesquicarbonate *v.* Natron; also Sodium.

TROPÆOLINE *v.* Azo- colouring matters.

TRUFFLE. The name of several kinds of subterranean edible fungi. That commonly sold in England is *Tuber æstivum*; in France it is mainly the more highly prized *T. melanosporum*, and in Italy it is most frequently *T. magnatum*. Occasionally other fungi are fraudulently substituted, such as *Chæromyces meandriformis*, or *Scleroderma vulgare*, the use of which may be attended with danger. The English truffle, *T. æstivum*, is usually about the size of a small apple, black outside, and brownish with streaks of white within. It has a strong penetrating smell, and is commonly found in beech, oak, and birch woods, associated occasionally with *T. brumale*, and in France with *T. melanosporum* and *T. mesentericum*. The French truffle, *T. melanosporum*, is brown or black in colour, and covered with coarse, polygonal warts, and has a pleasant smell, resembling that of the strawberry. It occurs mainly in oak and beech woods, in calcareous marly soils, and is gathered in autumn. The Italian truffle, *T. magnatum*, is brownish buff in colour, and has a strong alliaceous smell. The 'false truffle,' *Scleroderma vulgare*, is said to be gathered by Italians in Epping Forest, where it occurs on the surface of the ground, and is used in inferior dining-rooms in London. Other edible truffles are *T. brumale*, found in winter; *T. mesentericum*, found in summer; and the strong-smelling *T. macrosporum*, found in stiff argillaceous soils. The 'red truffle,' *Melanogaster variegatus*, is allied to the puff-balls, and is not a true truffle; it is brown in colour, and has a smell of bitter almonds. The smell of truffles is so strong that dogs and pigs may readily be trained to detect and dig them up. Truffles contain mannite, malic and citric acids, and fat. The characteristic odoriferous principle in truffles, although readily volatile, and passing over with water on distillation, does not appear to be an essential oil.

TSCHEN. Chinese coins of a brass or bronze-yellow colour, containing 55–64 p.c. copper, 26–35 p.c. zinc, and from 1–2 p.c. tin, 2–4 p.c. iron, and 1–6 p.c. lead; and occasionally small quantities of antimony, arsenic, and nickel (Pöpplein, C. C. 1859, 484).

TSCHEWKINITE $M''SiO_3M'''TiO_3$. A silicotitanate of iron and cerium, lanthanum, didymium, of a velvet black colour, found in the Ilmen mountains.

TSCHERMIGITE. Native ammonia-alum, first found at Tschermig in Bohemia.

TSE-HONG. A mixture of white lead, alumina, ferric oxide, and silica, used by the Chinese for painting on porcelain.

TSING-LIEN. A red pigment used in porcelain painting. Consists of a mixture of stannic and plumbic silicates with copper oxide or cobalt and gold.

TULA METAL. An alloy of silver, copper, and lead made at Tula in Russia.

TUNGSTEN. *Wolfram.* Sym., W. At. wt. 183·6 (Marchand, v. Borck, Dumas, Schleibler, Persoz, Roscoe); 184·04 (J. Waddell).

Tungsten occurs rarely as *wolfram ochre* or *wolframine* WO_3. Its principal ore is *wolfram* $2FeWO_4$, $3MnWO_4$ (the 'cal' of the Cornish miner), which is usually found with tin ores and with those of molybdenum, occurring principally in Cornwall, Devonshire, Cumberland, Sweden, and Bohemia. Tungsten is also found as *scheelite* $CaWO_4$, and *scheelinite* $PbWO_4$, and in the rarer minerals, *wolframite* $(MnFe)WO_4$ and *ferberite* $FeWO_4$.

Tungsten is prepared by heating the trioxide with carbon, or in a current of hydrogen, or by heating the chloride in the vapour of sodium.

It is a bright-grey metallic powder of sp.gr. 19·129 at 4° (Roscoe). It melts only at the strongest white heat. In air or oxygen it burns at a red heat, with formation of the trioxide. It combines with chlorine at 250°, forming the hexachloride; with bromine, forming the pentabromide; and with iodine, forming the diiodide. When heated, it combines with sulphur and phosphorus. On water it has no action, but when heated to redness it is converted by steam into a mixture of the blue oxide and the trioxide. It is attacked slowly by nitric acid, rapidly by aqua regia.

The presence of tungsten much increases the hardness and tenacity of steel, and generally improves its properties. The alloy is used for the preparation of hard tools. It resists atmospheric corrosion, damascenes finely, and is capable of taking a higher degree of magnetisation than other steel. According to Gruner (C. R. 96, 195), such steel is less affected by salt water. The tungsten (free from sulphur and arsenic) is added to crucible steel during the later stages of its manufacture. With 5–6 p.c. tungsten the steel is very hard but workable, but when the proportion reaches 10–12 p.c. it is so hard as to be unworkable with the lathe, and can only be forged or ground (D. P. J. 256, 570; C. C. 13, 782). Other alloys of tungsten are known, but are of no industrial importance.

Tungsten forms four chlorides and two oxychlorides: WCl_2, WCl_4, WCl_5, WCl_6, $WOCl_4$, WO_2Cl_2; with bromine it forms WBr_2, WBr_5, $WOBr_4$, WO_2Br_2, and with iodine WI_2, but no fluoride has been isolated.

Two sulphides, WS_2, WS_3, and sulphotungstates of potassium, K_2WS_4 and of sodium and ammonium, two phosphides, W_3P_4 and W_4P_2, a nitride W_3N_2, and two amides, $W_3H_6N_1$, $W_3H_1N_4$, are also known.

Tungsten dioxide WO_2 is produced by reduction of the trioxide at a carefully-adjusted dull-red heat, in a current of hydrogen. It is a brown powder, strongly pyrophoric when warm.

Tungsten trioxide WO_3. Finely-powdered wolfram is heated for a considerable time with hydrochloric acid, with the final addition of a little nitric acid to oxidise the iron. When all the iron and manganese are removed, the *yellow* residue, which consists of tungsten trioxide and a little quartz and undecomposed wolfram, is washed, and shaken with ammonia. The oxide is thus dissolved as ammonium tungstate, which is crystallised by evaporation and ignited, with reproduction of the pure trioxide.

The oxide is a fine bright canary-yellow powder, becoming orange coloured when heated, but returning to its original colour on cooling. On exposure to light, it acquires a greenish tinge. Roscoe has observed that the presence of a small quantity of sodium salt produces a permanent greenish tinge.

It is used as an oil and water colour, and appears to be quite permanent.

When heated to 250° in a current of hydrogen, the trioxide is reduced to a blue oxide $2WO_3WO_2$, which has been used as a pigment; at a dull-red heat the dioxide is obtained, and at higher temperatures metallic tungsten. It is acted upon by other reducing agents, such as zinc, in hydrochloric acid solution, stannous chloride, &c., giving first the blue and finally the brown oxide.

In alkalis and alkaline carbonates and ammonia, it dissolves, with formation of tungstates. It dissolves slowly in concentrated hydrochloric and hydrofluoric acids, but not in other acids.

Tungstic acid H_2WO_4. On addition of a cold acid to a cold solution of a tungstate, the white hydrated acid $H_2WO_4.H_2O$ is precipitated. This is soluble in water, bitter in taste, and acid to litmus. From hot solutions the anhydrous yellow acid is precipitated, insoluble in water, and in all acids except hydrofluoric acid. A colloidal tungstic acid has been prepared by Graham.

Alkaline tungstates are soluble in water. All tungstates are insoluble in alcohol, and are decomposed by most acids.

Metatungstic acid $H_2W_4O_{13}.7H_2O$ is produced by decomposition of barium metatungstate by dilute sulphuric acid. It crystallises from water in small yellow octahedra, which become anhydrous at 100°, and produce the trioxide on ignition. The solution, when heated, deposits a white hydrate, and finally the trioxide.

Alkaline metatungstates may be prepared by boiling normal tungstates with tungsten trioxide until the solution is no longer precipitated by hydrochloric acid; the others may be prepared by decomposing the barium salt with the proper sulphate. Most metatungstates are easily soluble and bitter, giving no precipitates with acids, but on continuous boiling they deposit normal tungstic acid.

Potassium tungstates. Trioxide of tungsten is added in small portions to its own weight of fused potassium carbonate. On evaporating at ordinary temperatures the solution obtained by lixiviation of the fused mass, the anhydrous salt K_2WO_4 is obtained in large needles, or the hydrous salt $K_2WO_4.2H_2O$ in prisms. When the normal salt is boiled in but little water, the acid salt is deposited in glistening scales containing $K_{10}W_{12}O_4.11H_2O$. Two hydrated metatungstates, $K_2W_4O_{13}.5H_2O$ and $K_2W_4O_{13}.8H_2O$, and several polytungstates are also known.

Sodium tungstates. In addition to the normal salt $Na_2WO_4.2H_2O$, eight polytungstates, ranging from $Na_2W_2O_7.2H_2O$ to sodium paratungstate, $Na_{10}W_{12}O_4.28H_2O$, and the metatungstate $Na_2W_4O_{13}.10H_2O$ are known.

Normal sodium tungstate $Na_2WO_4.2H_2O$ may be prepared like the potassium salt. It crystallises in rhombic plates, soluble in 2 parts of hot and 4 parts of cold water, forming a solution of bitter taste and alkaline reaction. At 200° the crystals become anhydrous and opaque, and fuse at a red heat.

Sodium tungstate is prepared on the large scale, directly from wolfram, by Oxland's process. The wolfram, or dressed tin ore, having been assayed, is mixed with the required amount of soda ash to convert all the tungsten into sodium tungstate, and thrown in charges of 6–10 cwts. upon the cast-iron bed of a reverberatory furnace, and maintained at a good red heat for about four hours with frequent stirring. The semifused mass—which consists of sodium tungstate, unchanged tin oxide, oxides of iron and manganese, and a little silica—is then withdrawn, and broken into small lumps before cooling.

For lixiviation vats are used, below each of which is a receiver; before the plug-hole of each vat is a perforated iron plate, with a rough filter of tow or straw. The charge, while still hot, is thrown into the vats, which contain a small quantity of water, the vats being filled up with water when fully charged with ore. After a half-hour the plug is withdrawn, and the contents are run into the receiver, the residue being again treated. The lixiviate, when showing a density of over 25°Tw., is at once conveyed to the evaporating pans, but when below that strength is used for extracting the first charge of another vat.

The solutions are concentrated in iron pans to the crystallising point, and removed to the coolers, from which the deposited crystals are removed and drained, the mother-liquors being mixed with a fresh liquor for evaporation.

Sodium tungstate is used to replace sodium stannate as a mordant in dyeing and printing, especially for wool and silk, and is employed as a fireproofing material for wearing apparel. It has been used for decolourising acetic acid and acetates made from pyroligneous acid.

Many other tungstates are known. Lead tungstate, prepared by the precipitation of sodium tungstate with lead acetate, has been used as a substitute for white lead. It is, however, of somewhat uncertain composition, and is deficient in body. Tungstates of tin and zinc, and especially of barium, have been used for the same purpose.

Tungsten potassium bronze. 'Magenta bronze' $K_2W_4O_{12}$ is prepared by addition of tungsten trioxide to fused potassium tungstate so long as it dissolves. The whole is gently heated in a current of hydrogen, and digested successively with water, hydrochloric acid, potash, and water, leaving small violet crystals of coppery lustre. Or potassium polytungstate is fused with tin, and the resultant is treated first with caustic soda and then with hydrochloric acid. By the action of the electric current on potassium polytungstates, deep-blue coppery crystals are obtained, whose composition, according to Zellnow, is $K_2WO_4H_2O$ (compare G. v. Knorr, J. pr. [2] 27, 49).

Tungsten sodium bronze. 'Saffron bronze' $Na_2W_3O_9$ (Malaguti) or $NaWO_3$ (Phillip a. Schwebel) is prepared like the potassium salt. It forms beautiful, golden, cubic crystals, unattacked by alkalis or acids, except hydrofluoric acid (J. Philpp, B. 15, 499).

A mixture of the potassium and sodium bronzes has been used for the production of a *violet* pigment.

Phosphotungstic acids and phosphotungstates are known, corresponding to those of molybdenum. The phosphodecatungstate has been used as a precipitant for alkaloids (*v.* Molybdenum).

Silicotungstic acid $4H_2O.SiO_212WO_329H_2O$, and several of its salts, have been prepared.

TUNGSTEN BRONZE *v.* Tungsten.

TUNGSTEN YELLOW *v.* Tungsten.

TURF *v.* Fuel.

TURGITE *v.* *Iron oxides*, art. Iron.

TURMERIC (*Indian saffron*; *Terra merita*). The so-called turmeric root of commerce is the underground stem or rhizome of *Amomum Curcuma*, or of various species of Curcuma—*e.g.* *C. tinctoria*, *C. viridiflora*, &c. These plants, belonging to the *Scitamineæ*, are indigenous to Southern Asia, and are there largely cultivated, being exported from China, Madras, Bengal, Java, Malabar, Batavia, and Barbadoes. Those varieties which are derived from the central rhizomes are more or less round (*Curcuma rotunda*), while the lateral rhizomes are long and finger-shaped (*C. longa*). When of good quality these commercial varieties are hard, and of a dull, waxy, resinous fracture, the external colour being yellowish-grey, internally an orange-brown, but producing when ground a somewhat bright yellow powder, having a strong characteristic odour and a peppery bitter taste.

The rhizome of *Canna speciosa*, a West African plant, is said to be exactly similar to East Indian turmeric in taste, smell, and chemical reactions (Daniell, Ph. 19, 258). It is cultivated in Sierra Leone, and furnishes the so-called 'African turmeric.'

According to Pelletier and Vogel, turmeric contains cellulose, gum, starch, mineral matter, a strong-smelling volatile oil, a brown colouring matter, and a characteristic yellow colouring matter named by them *Curcumin*. Pectin and pectic acid are also present (Schützenberger). Kachler found a notable quantity of binoxalate of potash.

Pelletier and Vogel's method of isolating the curcumin was long and tedious, and consisted in first removing the fatty, resinous, and other impurities by successively extracting pulverised turmeric with water and carbon disulphide, then dissolving out the colouring matter with boiling alcohol, and purifying it by successive solution in ether and alcohol, precipitation with lead acetate, and subsequent treatment with hydrogen sulphide and extraction with ether. It was thus obtained as an amorphous yellow powder.

Lepage adopted a similar method, but after extraction with carbon disulphide the colouring matter was dissolved in alkali, precipitated with acid, and finally purified with ether.

Daube was the first to obtain curcumin in the crystalline state. He first removed essential oil by passing a strong current of steam over the coarsely-ground turmeric, then thoroughly extracted it with hot water, and finally treated the dried residue with boiling benzene. On cooling the solution thus obtained, crude curcumin separated as bright orange-red crystalline crusts, which, after pressing between blotting-paper, were dissolved in cold alcohol. After filtering off some yellow flocculent substance, the solution was precipitated with an alcoholic solution of neutral lead acetate, adding finally a little basic lead acetate in order to neutralise almost entirely the liberated acetic acid and prevent thereby any solution of the colour-lake. The brick-red precipitate was washed with alcohol, suspended in water, and decomposed with hydrogen sulphide. The liberated curcumin was extracted from the precipitate with boiling alcohol, from which it crystallised on slow evaporation.

Benzene is very suitable for obtaining pure curcumin, for although it is very little soluble in this liquid, the resinous matters which are soluble in alcohol and ether are totally insoluble therein.

Gajewsky obtained crystalline curcumin by first extracting turmeric root with carbon disulphide, then dissolving out the colouring matter with ether, and purifying it by fractional crystallisation from ether or benzene. He detected the presence of another colouring matter, also traces of an alkaloid. This chemist obtained a greater yield of colouring matter by washing the dry ethereal extract with dilute ammonia to remove resin, then dissolving the brittle residue in boiling concentrated ammonia solution and precipitating with carbon dioxide; 250 grms. ethereal extract gave 100 grms. flocculent curcumin, m.p. 140. Jackson also obtained crystallised curcumin by first removing the oil by long extraction with carbon disulphide (60 hours), then thoroughly extracting (60 hours) with ether, and after washing the orange-coloured extract thus obtained with cold alcohol or ether, crystallising from hot alcohol.

Pure curcumin crystallises from alcohol in the form of lustrous pale-yellow or orange-coloured prisms, frequently arranged in stellar tufts. It is very soluble in ether, also in alcohol, giving with the latter a fluorescent solution capable of reducing silver nitrate. It is slightly soluble in concentrated acids, but readily so, with a reddish-brown colour, in alkalis, from which solution it is precipitated unchanged by acids. With calcium and barium salts it gives reddish-brown precipitates, with lead salts a bright-red precipitate soluble in acetic acid. With potassium it appears to form two salts, a fiery red-coloured neutral salt and a dark crimson acid salt, obtained by adding ether to mixed alcoholic solutions of curcumin and potassium hydrate, one or other being in excess. Melted with caustic potash, curcumin yields protocatechuic acid. Complete oxidation of curcumin with potassium bichromate and sulphuric acid yields carbon dioxide and acetic acid. Fuming nitric acid gives oxalic and hydrocyanic acids. After incomplete oxidation by means of permanganate, acidifying with sulphuric acid, filtering, extraction of the filtrate with ether, and treating with sodium bisulphite, an oil is obtained partly congealing to fibrous crystals, m.p. 79°, and smelling strongly of vanillin.

Sodium amalgam decolourises an alcoholic solution of curcumin. Distilled with zinc-powder, curcumin yields a brown oil, b.p. 280–290°C., of aromatic odour, in which Kachler detected microscopic crystals similar in appearance to anthracene. In consequence of its colour reactions and the results of some of its analyses, this chemist thinks that curcumin may possibly be related to chrysophanic acid. The formula and constitution of curcumin are not yet definitely determined. Daube gives it the formula $C_{10}H_{10}O_3$, m.p. 165°C.; Gajewsky, $(C_4H_4O)_n$, probably $C_{16}H_{16}O_4$, m.p. 172°C.; Jackson, $C_{14}H_{14}O_4$ or $C_{28}H_{26}O_8$, m.p. 177–178°C.

Jackson and Menke have prepared the following curcumin derivatives.

Dihydrocurcumin $C_{14}H_{16}O_4$, m.p. 100°C. *ca.*, is obtained as a brownish-white powder by long standing of a dilute alcoholic solution of curcumin with sodium amalgam, and precipitation with hydrochloric acid.

Dihydro-curcumin-anhydride $(C_{14}H_{15}O_4)_2O$, m.p. 120°C. *ca.*, is obtained as a dirty-white powder by heating a glacial acetic acid solution of curcumin with zinc-powder, and precipitating with water.

Diethylcurcumin was obtained as a brownish-black tar by treating an alcoholic solution of di-potassium curcumin with ethyl iodide.

A mixture of *mono-* and *di- ethylcurcumin-dihydride* $(C_2H_5).C_{14}H_{15}O_4$ and $(C_2H_5)_2.C_{14}H_{14}O_4$, is obtained by the reduction of diethyl-curcumin with zinc-powder and glacial acetic acid. Oxidation of all these ethyl derivatives with permanganate of potash yields ethyl vanillinic acid, m.p. 195°.

Curcumin-mono-*p*-brombenzyl-ether $C_{14}H_{13}(C_7H_6Br)O_4$, m.p. 78°, is obtained as pale-yellow crystals by long standing of a mixture of an alcoholic solution of the acid potassium salt of curcumin, and *p*-brombenzyl-bromide. Other derivatives obtained by the above authors were a bromide of the formula $C_{14}H_{10}Br_4O_4$; *curcumin-tetrabromide* $C_{14}H_{14}Br_4O_4$, m.p. 185°C.; *penta-brom-curcumin-dibromide*, m.p. 120°C.; and *mon-acetyl-curcumin*; all amorphous substances. *Diacetyl-curcumin* was obtained as yellow rhombic tabular crystals, m.p. 154°C.

Turmeric oil is the thick, orange-coloured, aromatic oil extracted from turmeric to the amount of about 11 p.c. by means of carbon disulphide or ligroin. It is unsaponifiable apparently, and on distilling gives no pungent odour, as in the case of glycerol compounds. Bolley examined the portion distilling over at 230–250°C., and gave it the formula $C_{10}H_{14}O$. In consequence of it yielding with ammonium sulphide a crystalline compound, Bolley considered it to be identical with carvol. Flückiger regards this as an error, because of the differences in boiling-point and rotatory power of the two products. Gajewsky is of the same opinion, and finds that the portion distilling over at 220–228°C. contains less carbon and more hydrogen than that which passes over at a higher temperature. On oxidising the latter portion with chromic acid in the cold much gas is evolved, and an acid oil is obtained, b.p. 150–170°, which contains valerianic, caproic, and terephthalic acids.

Jackson and Menke analysed that portion of turmeric oil which distils over at 285–290°C. or 193–198° (60 mm.), and gave it the formula $C_{19}H_{28}O$ and the name *turmerol*. Heated with hydrochloric acid it yielded *turmeryl-chloride* $C_{19}H_{27}Cl$, a pale-brown odorous oil. By heating a mixture of turmerol and ligroin and adding sodium, *sodium turmerol* $C_{19}H_{27}ONa$ was obtained as a tough semi-solid mass, which by digestion with iso-butyliodide gave *turmerol-isobutyl ether* $C_{19}H_{27}OC_4O_9$, as a heavy, yellow, pleasant-smelling oil. Complete oxidation of turmerol with excess of permanganate gave terephthalic acid; incomplete oxidation yielded *turmeric acid* $C_{11}H_{14}O_2$, and *apoturmeric acid* $C_{10}H_{12}O_4$ or $C_{10}H_{10}O_4$.

The following interesting colour reactions of curcumin have long been known to chemists. Turmeric paper—*i.e.* white paper stained yellow with an aqueous or alcoholic extract of turmeric —is coloured by alkalis a brownish-red, which assumes on drying a violet hue; the original yellow is entirely restored by dilute acids. Boric acid solution changes the colour of turmeric paper to a pure bright orange-red, fully developed only after drying, and quite distinct from that given by alkalis. It is unchanged by dilute acids, becomes red by the action of strong mineral acid, *e.g.* hydrochloric or sulphuric acid, and is changed by alkalis to blue, which rapidly changes to a dirty grey. Schlumberger studied this reaction, and found that on boiling an alcoholic solution of curcumin with boric acid it acquired an orange colour; if water was then added to the cold solution, there was precipitated a vermilion-coloured compound containing boric acid, insoluble in water, ether, and benzene, but very soluble in alcohol, with an orange colour. This substance is very unstable, and is decomposed either by the prolonged action of water, or immediately if its alcoholic solution is boiled; the boric acid dissolves, and leaves behind a yellow resinous matter, *pseudo-curcumin*, which differs from curcumin in that it does not give a red colouration with hydrochloric and boric acids, and that it gives with alkalis a greenish-grey colouration. The vermilion-coloured boric acid compound of altered curcumin dissolves in alkalis, with a purplish-violet colour soon turning to grey. If the orange-coloured alcoholic solution of this compound is boiled with the addition of hydrochloric or sulphuric acid, or if an alcoholic solution of curcumin, with addition of boric and sulphuric acids, be boiled, the solution acquires a deep-red colour. The reaction is complete whenever a sample of the liquid becomes blue on the addition of ammonia. If now the solution is cooled, a new substance, *rosocyanin*, separates out as a dark granular substance, while boric acid remains in solution. When purified, by first washing with dilute alcohol and water to remove boric acid, and then crystallising from a mixture of alcohol and acetic acid, and washing with ether, rosocyanin forms dark-red needles having a green metallic lustre. It is insoluble in water, ether, and benzene, but very soluble in alcohol, with a deep magenta colour, which changes to an evanescent bright blue colour by the action of ammonia, and to a yellow colour (pseudo-curcumin) on boiling the solution; 100 grms. of an alcoholic extract of turmeric yield 15 grms. rosocyanin. It contains no boron, and on melting with caustic potash yields paraoxybenzoic acid. In its general chemical properties, rosocyanin resembles cyanin, the colouring matter of flowers, but their constitution and relationship to each other are entirely unknown.

Employment.—Turmeric has long been used in India and China in the dyeing of cotton and silk, employing a decoction slightly acidulated with 'lime juice.' It has also been and even now is still used in Europe, sometimes to dye cotton yellow, but chiefly to furnish the yellow part of compound colours on wool (*e.g.* 'sour browns,' *v.* SANDERSWOOD), and also on silk. It is applied in an acid bath, along with indigo-extract, orchil, &c. Its chief characteristic as a colouring matter is that it dyes cotton direct, *i.e.* without the aid of any mordant. It gives a bright yellow, but one which is very sensitive to alkali, and extremely fugitive to light. Other uses of turmeric are for the colouring of lac-varnish, leather, wood, paper, cheese, oils, fats, &c.; it also forms one of the ingredients of curry-powder and other condiments. An alcoholic tincture of turmeric, and paper or calico stained with its aqueous or alcoholic extract, serve as a test for alkalis and for boric acid. Tuchschmidt recommends turmeric paper for determining within a half per cent. the amount of caustic soda in the presence of sodium carbonate. A solution containing both forms of alkali colours turmeric paper a yellowish-red, but whenever, by addition of acid to the solution, the last traces of caustic alkali are neutralised, the colour changes to carmine-red. The sodium carbonate can then be determined as usual. F. Watts recommends the use of an alcoholic turmeric tincture for the alkalimetric determination of citric acid in 'lime juice.'

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TURMERIC ACID *v.* TURMERIC.

TURMERYL CHLORIDE *v.* TURMERIC.

TURNBULL'S BLUE. A variety of Prussian blue, *v.* CYANIDES.

TURNER'S YELLOW. *Patent yellow.* Lead oxychloride $3PbO.PbCl_2$.

TURPENTINE *v.* OILS, ESSENTIAL; also TURPENES.

TURPENTINE VARNISH *v.* VARNISH.

TURPETH or **TURBITH MINERAL.** An old name for basic mercuric sulphate $HgSO_4.2HgO$, sometimes called Queen's yellow, *v.* MERCURY.

TURPETH or **TURBITH ROOT.** The root of *Convolvulus Turpethum* or *Ipomœa Turpethum*, found in India and Australia. It contains a volatile oil and a drastic resin, *turpethin* $C_{34}H_{56}O_{16}$, isomeric with jalapin and scammonin. When treated with dilute mineral acids this body is hydrolysed into glucose and *turpetholic acid* $C_{16}H_{32}O_4$ (*v.* Boutron-Charlard, J. Ph. 8, 131; Spirgatis, J. pr. 92, 97).

TUTENAG or **TUTENAGUE.** *Chinese silver. Packfong.* An alloy resembling German silver.

TYPE METAL *v.* TIN.

TYRIAN PURPLE *v.* MUREX; also PUNICIN.

TYROLITE. *Pharmacosiderite. Cupriferous calamine. Copper froth* $Cu_3As_2O_8.2CuH_2O_2.7H_2O$. A basic copper arsenate, of an apple green or verdigris-green colour, found in the Tyrol.

TYROSINE $C_6H_4(OH)CH_2.CH(NH_2)CO_2H$. A substance first obtained by Liebig by fusing cheese with potash (A. 57, 127; 62, 269). May also be obtained from horn, feathers, hair, and various albuminoids by boiling with dilute sulphuric or hydrochloric acid. Found in moths, caterpillars, spiders, and crayfish. Occurs, accompanied by leucine, in the spleen and pancreas; in the liver and in the blood of the hepatic veins in certain conditions of liver disease; in the bile of typhus patients, and occasionally in urine. Best prepared by boiling horn shavings with dilute sulphuric acid (for details *v.* Hinterberger, A. 71, 74; Städeler, A. 91, 12).

Tyrosine crystallises in fine lustrous needles, which dissolve in 2,400 parts of cold water and 150 parts of boiling water. Very sparingly soluble in cold alcohol; insoluble in ether. Has a neutral reaction, but combines both with acids and bases.

U

UARANA *v.* GUARANA.

ULEXITE. *Boronatrocalcite v.* BORON; also *Borax*, art. SODIUM.

ULTRAMARINE. Ultramarine was not artificially made until the year 1828, when Guimet discovered a method of producing it on a commercial scale, and thus earned the prize of 6,000 francs offered by the 'Société d'Encouragement' of France for its production at a cost not exceeding 90*s.* per lb. About the same time the discovery was independently made by Gmelin, who published his method.[1] Ultramarine exists in nature in the form of lapislazuli, but its scarcity, and the cost of extracting the colour from the mineral, rendered its practical use as a pigment impossible.

The formation of ultramarine in small spots had frequently been observed by alkali manufacturers in the produce of the soda kilns, and this had led to many unsuccessful attempts to produce the colour in quantity.

The exact chemical composition of ultramarine is still a matter of uncertainty, and although its analysis is simple and its constituent parts easily ascertained, there is much in the manufacture depending upon the results of experiments, and but little upon the application of theory.

The colour can be made in such a variety of shades and tints, possessing such different degrees of tinctorial power, and the proportions of silica and alumina may differ so widely, that the assumption would seem to be well justified that this body is the result partly of chemical combination and partly of mechanical mixture. Certainly, ultramarines have not yet been shown to possess a uniform composition, and even with repeated operations, in which exact amounts of raw materials are used and similar conditions as far as possible secured, the results vary both as to appearance and analysis.

Ultramarine is, probably, a double silicate of sodium and aluminium, together with bi-sulphide of sodium. R. Hoffmann (A. 194, 1–22) considers that the kind poor in silica and of a pale pure tint has the formula $4(Al_2Na_2Si_2O_8) + Na_2S_4$, while the kind rich in silica and of a deep reddish tint consists of $2(Al_2Na_2Si_3O_{10}) + Na_2S_4$. The former he presumes to come from white ultramarine by the removal of three molecules of sodium from four molecules of the white ultramarine of its series; and the latter by the removal of three of sodium from two molecules of the white of its series. He, therefore, makes the formula of white ultramarine poor in silica

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[1] According to Heintz (J. pr. [2] 43, 98), the discovery of ultramarine is due to Koltig, the director of the laboratories of the Konigl. Porzellan-manufaktur in Meissen.

$$4(Na_2Al_2Si_2O_8 + Na_2S),$$

in which series red and yellow compounds have been made, but not much investigated. Of the series rich in silica the white ultramarine has not yet been made, and all attempts to make it have failed, the green is little known, and even the blue is not equal in purity of tint to that poor in silica. Proceeding by deduction, Hoffmann proposes as the formula of the undiscovered white ultramarine

$$2(Na_2Al_2Si_3O_{10} + 2Na_2S).$$

In this series there are also red and yellow varieties. The red may be made from blue by passing dry hydrochloric acid gas over it at a temperature of 150°, admitting air. A violet colour first appears, which becomes after a long continuance of the operation an intense rose red, without the liberation of hydrogen sulphide or other sulphur acids in any considerable quantities. The whole of the sulphur of the blue ultramarine appears to pass into the new compound. On washing, sodium chloride and some alumina are dissolved. Hoffmann infers from his observation of the behaviour of red ultramarine that it is not under the most favourable circumstances so chemically pure as the blue.

Grünzweig found that yellow ultramarine rich in silica can be made with certainty, and, proceeding from the blue, the formula is derived by abstracting one-fourth of the sulphur and adding oxygen equivalent to the total sulphur in the blue ultramarine. The result is

$$2(Na_2Al_2Si_3O_{10}) + Na_2S_3O_4.$$

The yellow is thus an oxidation product of the blue.

Hoffmann was the first to discover that ultramarine is a crystalline body. A crystalline appearance had been before noticed, but attributed to uncombined quartz sand. The crystals are chiefly single refracting, and belong to the regular system. This has been confirmed by other observers.

Böttinger (A. 182, 305) considers that ultramarine may be looked upon as the last term of a series of molecular compounds of an aluminium silicate, with a sodium silicate in which the oxygen is more or less replaced by sulphur.

Wilkins argues that it consists of two parts, one of which is a combination of two silicates of alumina with sulphite and sulphide of sodium, constant in composition, while the other is a mixture of variable quantities of sand, clay, and oxide of iron, with sulphuric acid.

Fürstenau (D. P. J. 219, 269) gives the following compositions.

A pure clear blue with little colouring power, $4Al_2O_3,9SiO_2$ with Na_2S.

A pure dark blue with great colouring power, $4Al_2O_3,9SiO_2$ with Na_2S_5.

A light-reddish dingy blue, $Al_2O_3,3SiO_2$ with Na_2S_2.

A dark-violet blue with great colouring power, $Al_2O_3,3SiO_2$ with Na_2S_5.

Ritter holds that ultramarine contains a double silicate, not only associated with polysulphide, but also with thiosulphate of soda, while Brunner considers it a compound of aluminium silicate with sodium sulphate and sulphide.

Unger (B. 5. 989) states that ultramarine contains nitrogen, and has the composition

$$Al_2SiO_2O_3N_2,$$

the sodium used in the manufacture being eliminated in the course of the reaction as sulphide and sulphate. The nitrogen he supposed to be partly derived from the air.

Endemann believes that the blue colour is due to a 'colour nucleus' consisting of unchanging proportions of aluminium, sodium, oxygen, and sulphur in each variety of ultramarine, the proportion being different, while the rest of the sodium and aluminium, and the whole of the silica, merely act as a vehicle necessary to the preparation and existence of the colour. He considers that this 'colour nucleus,' in the case of white ultramarine, which he calls 'the mother substance in the manufacture of blue ultramarine,' has the formula $AlNa_4O_2S_2$. By acting upon two molecules of this with sulphurous acid Na_2O is removed, and green ultramarine $Al_2Na_6O_3S_4$ formed. This green, by the action of oxygen, which forms sodium sulphate, passes into the pure green compound having the formula

$$Al_2Na_4O_3S_3.$$

G. H. Philipp (A. 191, 1–12), in comparing blue and green ultramarines, finds that the latter may be converted into the former by heating in a sealed tube with water at 100°, and concludes that the conversion is due to the oxidation of sulphur to SO_2 or S_2O_2. It has also been contended that the conversion is due entirely to the water dissolving a small amount of sodium sulphide, the composition of the colour remaining unaltered. Philipp (D. P. J. 231, 500–503) considers that blue and green may be distinguished by the amounts of sodium sulphide present.

R. Rickmann (Ber. 11, 2013–2017) thinks that when ultramarine white $2(Na_2Al_4(SiO_4)_2)Na_2S$ is converted into blue by roasting with sulphur, the sulphurous acid combines with sodium and aluminium, liberating silicic acid, which in the nascent state unites with sodium sulphide, forming sodium sulphosilicate $S.Si(ONa)_2$, or 'ideal ultramarine blue.'

Rickmann also gives it as his opinion (D. P. J. 232, 164–176) that artificial ultramarine is not a chemical individual but a mixture of compounds, one of which is essential to its constitution, the others being by-products. The essential compound he takes to be sodium sulphosilicate.

From a chemical point of view silver ultramarine is perhaps the most interesting variety yet discovered, not alone upon its own account, but because it forms a starting-point from which many other kinds can be made. It is a dark yellow amorphous body, and was first obtained by Henman (B. 10, 991) by heating blue ultramarine with a solution of silver nitrate in a sealed tube at 120° for fifteen hours. In this body two-thirds of the silver exist as aluminium silver silicate, and one-third as silver sulphide.

On fusion with potassium iodide, the silver ultramarine is converted into potassium ultramarine of a clear blue colour. Fused with lithium iodide, a lithium ultramarine is produced resembling the corresponding compounds of sodium and potassium, and of a beautiful blue colour. By heating this with sulphur in a current of air, the colour is changed first to green and then to pink, and a red compound is obtained by heating in a current of hydrochloric acid, gas, and air. If silver ultramarine is heated with sodium chloride, the silver is replaced by sodium, and by acting with the corresponding salts the following are obtained: barium-ultramarine, a yellowish brown; zinc ultramarine, a violet; and manganese ultramarine, a grey. In addition to the compounds already mentioned ultramarines can be made with organic radicles; thus benzyl-, amyl-, and ethyl- ultramarines have been made by acting upon the iodides in a sealed tube at 180°. Ethyl ultramarine is a greyish-yellow powder. If heated with sodium chloride it turns blue, ethyl sulphide being given off, the sodium taking the place of the ethyl and forming ordinary blue sodium ultramarine. There is apparently great diversity in the composition of ultramarines manufactured by slightly different methods, still further complicating the problem of the chemical composition of this body. Differences might be expected between the kinds poor and rich in silica, but they extend in a remarkable degree to those supposed to be similar in composition. The following are some analyses of different makes rich in silica:—

——	SiO_2	Al_2O_3	Na_2O	S	Total
1. German manufacture . . .	38·90	29·50	21·02	10·84	100·26
2. German manufacture . . .	39·61	23·95	19·15	13·10	101·66
3. English manufacture . . .	42·70	24·50	19·95	13·04	100·19
4. German manufacture, violet .	41·30	24·30	17·40	14·80	101·30

The behaviour of ultramarines with various reagents has been carefully studied, but, though interesting, the facts observed do not appear to lead to a much deeper knowledge of the subject.

Concentrated and even dilute mineral acids rapidly decompose all kinds of ultramarine, with evolution of a part of the sulphur as sulphuretted hydrogen and the precipitation of the remainder; and the stronger organic acids have the same effect. Solutions of caustic potash or soda, whether hot or cold, do not alter green or blue ultramarine, but violet becomes blue. With sodium sulphide the blue and violet are unchanged, but the green turns grey. Heated to low redness, blue loses its brilliancy, and becomes greenish, while violet becomes blue passing on to greenish. Heated with carbonic acid, blue and green are unaltered, and violet becomes blue. With hydrogen at a high temperature blue becomes brownish yellow, and violet blue, and with potassium chlorate green turns darker and loses brilliancy. With chlorine at a low red heat green becomes bluish violet, and violet pink, while blue changes to violet. With dilute nitric acid fumes violet is converted into red.

Blue and green ultramarines are the only varieties of commercial interest. The yellow, white, red, and violet are interesting from a chemical point of view, but are not produced upon the large scale, though many efforts have been made to produce violet and red, and small quantities have been sold, but the colours have little tinctorial value, and are of little or no practical value. Leltner, of Nürnberg, obtained a patent for manufacturing red ultramarine. He passed chlorine gas and steam over blue ultramarine at a high temperature. Büchner has obtained red variety without the use of steam, and he states (D. P. J. 231, 466) that he has succeeded in making red and yellow ultramarines by using a smaller quantity of sodium in the mixture.

The blue ultramarine of commerce was for a long time solely made by what is called the 'indirect process,' and a good deal is still so made. Sulphate of soda, china clay, and carbon are ground together and burnt in crucibles, in an oven of a suitable form, for from six to nine hours at a red heat. On turning out the crucibles, the raw ultramarine is found to be of a somewhat dull green. This is crushed and placed upon a roasting furnace heated to a dull red, and there burnt with powdered sulphur, the mass being turned over constantly, until the sulphur has burnt off and the whole has assumed a bright-blue colour. This method produces only the kinds poor in silica, and though very pure in tint the depth and strength of colour are not great. The raw materials are cheap, and the loss in weight by heating small, but there is less certainty as to result, and the labour bears a high proportion to total cost. For these reasons this method has gradually been given up in favour of the 'direct process.' The selection of raw materials for this method is a matter of greater care, and, though the results are perhaps more certain, they depend upon a greater attention to detail. The mixture consists of about 100 parts of china clay, 90 of soda, 110 of sulphur, 20 of charcoal, and some infusorial earth, the exact amount depending upon whether the ultramarine is to be rich or poor in silica. The china clay must contain as little impurity as possible, must be very fine, free from rough sandy or stony matter, and should contain a high percentage of silica. The soda used is the best soda ash, known as carbonated ash, and should test 58 p.c. The raw materials, having been intimately mixed, are very finely ground together, and are then ready for burning. Two kinds of ovens are now in use, namely 'crucible' and 'mass' ovens, the latter being the newer, and, as many manufacturers consider, the better, plan. In working the former plan, the ground mixture is filled into crucibles of from twelve to sixteen inches high, lids are fixed on with a mortar made of clay, and the crucibles piled up in regular rows in the oven, which generally holds several hundred. The heat is slowly raised to a bright red, at which it is maintained until the burning is ended, the duration of time depending upon the size of the crucibles and the particular mixture. The oven is then closed, air being as far as possible excluded, and left to cool, after which the crucibles are removed, and the crude ultramarine—which presents a beautiful deep-blue colour—turned out and carefully scraped and chipped free from any over-burnt portions, and thus prepared for the washtubs. The 'mass' oven, so called from the mixture being treated in a mass, is now probably more used than the older kind, and produces very good ultramarine if carefully managed. Fig. 1 gives an idea of the arrangement. The raw materials, well mixed and ground, are shovelled on to the floor of the oven, pushed up to the end with a broad rake, and, after being piled up to nearly the level of the bridge, are neatly flattened, and covered with thin tiles, the joints being filled in with a very thin mortar made with china clay and sand. The oven having been thus filled, the front is built up, leaving a hole just above the level of the tiles for observation, fitted with a loose brick. A small hole below this and about opposite the centre of the mass, fitted with a clay stopper, affords a means of taking samples as the burning proceeds. The heat is slowly raised to a bright red, and as it rises small jets of sulphurous acid are seen to come from the cracks between the covering tiles and burn with feathery flames, increasing in length as the heat becomes greater, and gradually dying away as the reaction is completed. The heat is maintained at its highest point for from twelve to eighteen hours, or until the process appears to be finished, when a sample is taken through the small hole by means of a long auger inserted right into the middle of the mass. The sample presents, if sufficiently burnt, a greenish-blue appearance, gives off sulphurous acid freely without actually burning, and on being spread upon a clean tile quickly loses its heat, and appears a blue colour with a tinge of green. The changes gone through by the mixture are interesting and remarkable. It goes in a yellowish grey, and becomes successively brown, green, and blue. The brown, a dark-rich colour, is very unstable, and burns on exposure to air to a greenish half-formed ultramarine, and, even if not exposed, slow combustion goes on until oxidation has taken place. The green is almost equally unstable.

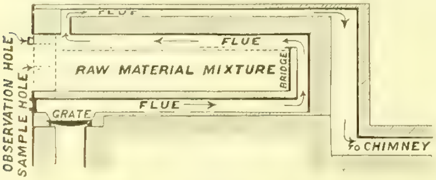

FIG. 1.

If the drawn sample be found sufficiently burnt, the operation is concluded by closing the oven, plastering up cracks, and excluding the air as far as possible. It is then left to cool down, which takes a week or ten days, and on opening, the mass should appear dark blue, the bottom portion not being quite equal in brilliancy to the top owing to the greater degree of heat to which it has been subjected. On weighing, a loss of about one-third of the original weight will be discovered, and it will also be noticed that the mass has considerably sunk. The ovens usually contain about one ton of raw material. The crude ultramarine having been removed from the oven, the inferior part being kept by itself, is taken to the washing vats. These may be of any convenient size, and have perforated false bottoms over which is stretched a rough filtering medium, allowing the water to pass through while retaining the pigment. The vats are filled nearly to the top with colour, and hot water run through slowly, until the free sulphate of soda, of which the raw ultramarine contains about fifteen p.c., is dissolved out. The washed colour is ground wet in upright mills between hard stones until the requisite fineness is attained. It is then drawn off, allowed to stand for a short time in a vat until the dirt and unground particles are deposited, and afterwards by careful settlement divided into different degrees of fineness. The first deposit is coarse, and contains sodium sulphide and other impurities; the second is coarse and dark, but quite clean; the third is lighter and finer, until at last the ultramarine is so finely ground and of such light specific gravity that it takes several weeks to fall. The valuable part of the colour having now been obtained, and further settlement being impracticable, the remainder is precipitated with lime, which coagulates the particles, and renders their removal by filtration easy. As the process of settlement continues, the colour becomes lighter, finer, bluer, and stronger, and the manufacturer finds by experience how best to regulate it so as to give the shades required. The blue is dried on kilns, and sifted through brass wire of one hundred to one hundred and forty meshes to the inch, being driven through the wire by a fan, by which means the lumps are broken up into a fine powder. All coarse particles or foreign matter pass out through the tail end of the sieve. The manufacture is now completed, and nothing remains but to mix together the various shades and sorts to produce the standards of sale. This part of the work is, however, of much importance, as the tinctorial power, fineness of grind, and depth and purity of colour in each standard, have to be exactly reproduced in each bulk.

Ultramarine is extensively used in a variety of manufactures. Its large consumption is consequent upon its two chief characteristics: brilliancy as a body colour, and high colouring power. As a body colour it is used in calico-printing, blue printing ink, wall-paper printing, blue writing paper, paint, and blue mottled soap, in which industries it plays an important part. As a 'whitening' agent it is very valuable, its great strength and purity of tone correcting the yellow tinge in writing and printing papers, finishing cotton and linen goods, sugar refining, &c., and giving a perfectly white appearance. In the manufacture of square and ball blue for laundry use, ultramarine is now very largely used, this branch of the industry having grown rapidly during the last fifteen years.

The development of the manufacture of ultramarine has been remarkable. The price the year after its discovery was about 16*s.* per lb., but competition soon brought this down, and created a demand. Guimet commenced the manufacture in 1828. Between 1830 and 1840 two other manufactories were started; 1840 to 1850 nine; 1850 to 1860 nine; 1860 to 1870 at least a dozen; and from 1870 to 1888 four or five more, and four or five have been closed. Germany has now about twenty factories, France six, United States three, England four, Austria two, and Belgium one. The number of men employed in the manufacture is perhaps two thousand five hundred, and the produce probably approximates ten thousand tons annually, though it is impossible to get any trustworthy or definite information upon this point. The rapid progress of the manufacture had the natural effect of gradually reducing the value of ultramarine, and the average price has sunk to under 30*s.* per cwt., a price which has stimulated the trade, opening up new sources of consumption, and causing the output to be increased.

This development is remarkable, especially when taken into account with the, as yet, imperfectly understood chemistry of ultramarine. Each year adds something to the accumulated experience, and improvements are from time to time made in the manufacture, but they are based more upon experiment than upon inductive reasoning. G. W. R.

ULTRAMARINE, GREEN, *v.* ULTRAMARINE; also CHROMIUM.

ULTRAMARINE, YELLOW. *Barium Chromate v.* BARIUM; also CHROMIUM.

UMBELLIFERONE *v.* GUM RESINS.

UMBELLULIC ACID *v.* FATTY ACIDS.

UMBER. A brown pigment, consisting of a mixture of the hydrated oxides of iron and manganese, mechanically associated with a large proportion of earthy matter of variable character. The material is prepared for the market by grinding and levigation. Raw umber is imported from Cyprus, Turkey, and Italy; while it is also worked to a limited extent in the United States.

Prof. A. H. Church gives the following analysis of a choice sample of raw umber from Cyprus: water, given off at 100°C., 4·8 p.c.; water expelled at a red heat, including organic matter, 8·8; Fe_2O_3, 48·5; MnO_2, 19; CaO, 1·4; MgO, 0·5; Al_2O_3, 2·1; P_2O_5, 0·9; SiO_2, 13·7; CO_2, &c., 0·3. Part of the manganese probably exists as Mn_3O_4 (The Chemistry of Paints and Painting, 1890).

For other analyses of umbers, siennas, and ochres, *v.* G. H. Hurst in C. N. 59, 1889, 172. He found crude Derbyshire umber to yield the following results: hygroscopic water, 13·475 p.c.; combined water, 5·175; $BaSO_4$, 30·105; SiO_2, 4·430; $CaSO_4$, 2·153; $CaCO_3$, 2·607; Al_2O_3, 8·078; Fe_2O_3, 22·500; MnO_2, 11·530. Hurst regards most ochres as alteration products, formed mainly by the oxidation and hydration of pyrites *in situ*, and mechanically mixed with silica, clay, and other earthy matter. Umbers may have been washed as a fine sediment from deposits of iron and manganese ores. The pigment termed *burnt umber* is merely umber which has been exposed to heat, whereby its colour becomes somewhat reddened.

F. W. R.

UPAS ANTIAR *v.* ANTIAR RESIN.

UPAS TIEUTÉ *v.* NUX VOMICA.

URACONITE *v.* URANIUM.

URANITE *v.* URANIUM.

URANIUM. Sym., U. At. wt. 239·8 (Péligot); 238·96 (Zimmermann).

This metal occurs principally as the oxide UO_22UO_3 in *pitchblende*, which is found in Cornwall, Joachimsthal, Saxony, Norway, and the United States. As sesquioxide, it is found associated with pitchblende in *uraconite* or *uranochre*. It occurs as phosphate in *uranite* or *uranium mica*, as phosphate of uranium and lime in *autunite*, as phosphate of uranium and copper in *torbanite*, as carbonate of uranium and lime in *liebigite*, and in *trögerite*

$$3UO_3As_2O_512H_2O,$$

uranospherite $Bi_2O_4UO_3H_2O$, and *samarskite*.

An important source of uranium compounds has been opened out, within the last two years, in the 'uranium mine' at St. Stephen's in Cornwall. During this period, the reduction works of this company, under the management of Mr. Kitto, has turned out considerably over a ton of the pure uranates of sodium and ammonium. The ore occurs as a well-defined lode containing *uranochre*, together with *pitchblende* and phosphates, arsenates, and other salts of the metal.

Uranium has been obtained by reducing uranous chloride with sodium. The compact metal is malleable and silver white, resembling nickel in colour. Its sp.gr. compared with that of water at 4° is 18·7 (Zimmermann); it melts at a bright-red heat. In air or water it is unaffected at ordinary temperatures, but it burns with formation of the green oxide when the powder is heated to 207°. It combines directly with chlorine and sulphur.

Uranium belongs to the chromium group of metals. It forms two principal oxides UO_2 and UO_3. The former is basic and is known as 'uranyl,' while the trioxide is regarded as its oxide, and forms uranic or 'uranyl' salts and uranates. Oxides intermediate between these; a black oxide UO_2UO_3, and a green oxide UO_22UO_3, are also known. Oxides containing less oxygen than UO_2, and a higher oxide UO_4, which forms *peruranates*, also appear to exist, but they have not been fully examined.

The *black oxide* UO_2UO_3 is best prepared by strongly igniting uranium nitrate. It is highly prized as a means for producing a pure intense black glaze on porcelain.

The *green oxide* UO_22UO_3 is obtained by heating the black oxide at a moderate heat in air or oxygen, or by heating uranium nitrate or ammonium uranate at a heat not high enough to reduce it to the black oxide. It is employed for producing the black glaze on porcelain, as is also the powdered native oxide *pitchblende*.

Sodium uranate is obtained by precipitating a uranic salt with excess of sodium hydrate, or by fusing uranic oxide with sodium carbonate. On the large scale, a mixture of 100 parts of pitchblende (containing about 45 p.c. UO_22UO_3) with 14 parts of lime, is roasted in a reverberatory furnace. The calcium uranate so formed is decomposed by dilute sulphuric acid, and the solution of uranic sulphate obtained is treated with sodium carbonate, the uranium and other metals being precipitated, the former re-dissolving in excess. The clear solution is just neutralised with dilute sulphuric acid and boiled, with precipitation of a finely-divided hydrated sodium uranate $Na_2U_2O.6H_2O$. This salt, known as 'uranium yellow,' is used for painting and staining glass and porcelain, and for making the fluorescent 'uranium glass.'

On addition of ammonium chloride or sulphate to a boiling solution of sodium uranate, a precipitate of *hydrated ammonium uranate* is obtained, which, when dried and gently heated, is also sold as 'uranium yellow.'

Many other uranates are known, but are of no industrial importance.

Uranium forms three chlorides and an oxychloride: U_2Cl_6, UCl_4, UCl_5, UO_2Cl_2 (uranyl chloride); with bromine it forms U_2Br_6, UBr_4, and UO_2Br_2, and with iodine UI_4. With fluorine several compounds have been prepared: UF_4; UO_2F_2; U_2O_2F; U_2OF_2; U_2O_3F; U_2F_34HF; and a fluoxyuranate of potassium UO_2F_23KF. Two sulphides and an oxysulphide are known: US_2, U_2S_3, and UO_2S.

Uranic or uranyl nitrate $UO_2(NO_8)_2.6H_2O$ is prepared by the solution of any uranium oxide in nitric acid. It crystallises from solution, in lemon-yellow, fluorescent, rhombic crystals. It is soluble in alcohol and ether, and is best purified by crystallisation from the latter. This salt is precipitated by solutions of phosphates and arsenates, and is used on that account for the estimation of phosphoric acid, and of arsenic after oxidation to arsenic acid. It is also used in photography, and has been proposed as a mordant in calico-printing.

Uranic or uranyl acetate $UO_2(C_2H_3O_2)_2.2H_2O$ is prepared by dissolving in warm acetic acid the yellowish-red mass produced by heating uranium nitrate until evolution of oxygen commences. It crystallises from the solution in yellow monoclinic crystals. It is used for the same purposes as the nitrate. Many double uranium acetates are also known.

Among other uranium salts may be mentioned the uranous and uranic sulphates $U(SO_4)_28H_2O$ and $UO_2SO_43H_2O$; phosphates; arsenates, of which several occur as minerals; and carbonates.

URANIUM MICA. *Uranite v.* Uranium.

URANIUM YELLOW *v.* Uranium.

URANOCHRE *v.* Uranium.

URANOSPHÆRITE *v.* Uranium.

URAO. A native form of sesquicarbonate of soda $Na_4H_2(CO_3)_2.2H_2O$, found in South America and other places.

URARI *v.* Curara.

USNIC ACID $C_{18}H_{18}O_7$ (Stenhouse, Pr. 18, 222), $C_{18}H_{18}O_8$ (Paterno, B. 9, 345). An acid found in certain lichens (*v.* Lichens).

UVITONIC ACID *v.* Bone oil.

V

VAL D'ARNO SUPERIORE RESIN *v.* Resins.

VALENTINITE. Native antimonious oxide Sb_2O_3 *v.* Antimony.

VALERIAN. The root of *Valeriana officinalis* yields on distillation with water an essential oil of a pale-yellow or greenish colour, having a strong smell of valerian, an aromatic taste, and acid reaction; sp.gr. 0·90–0·93. Thickens at −15°, and begins to boil at about 200°. Consists of a mixture of valeric acid, a camphene, a stearoptene, and a resin (Pierlot, A. Ch. [3] 56, 291; Gerhardt, A. Ch. [3] 7, 275).

VALERIANIC or **VALERIC ACIDS** *v.* Fatty acids.

VALONIA. The valonia trade has become of great importance to Smyrna, and the collection and sorting of the fruit occupy a large number of people in the interior. The valonia oak (*Quercus Ægilops*) grows wild on high sheltered mountain slopes. The crop depends largely on the heat of the season and the amount of rain. The quality, *i.e.* the percentage of tannin, depends on the season, only favourable and uniform weather giving good results. The harvest yields from four to eight hundred thousand centners. The middle sorts go mostly to England, the best to Austria and Lombardy. The following sorts are known to commerce:—

	Fr. per 100 kilos.
Uso Trieste	50 to 60
Cribbee	45 ,, 50
Unaqu	40 ,, 45
Naturale (uso inglese) . .	34 ,, 40
Refuso (1st and 2nd) . .	20 ,, 25

According to the quality, more or less refuse is mixed with the acorns. Landerer points out that at all the shipping places, as well as at the drying places in the woods &c., many hundred centners of small fruit are wasted or burnt for firing, from which an extract could profitably be prepared for exportation. One or two kilos of extract would contain the tannin of a centner of raw material (S. C. I. 2, 277), *v.* Leather; also Tannins.

VANADINE *v.* Vanadium.

VANADINITE *v.* Vanadium.

VANADIUM. Sym., V. At. wt. 51·1 (Roscoe). Minerals containing vanadium in quantity are rare, but the metal is widely distributed in small quantities.

Vanadium occurs as vanadic acid in *vanadine* with the native copper of Lake Superior; as lead vanadate and chloride in *vanadinite*; as lead pyrovanadate in the rare mineral *descloisite*; as hydrated vanadate of lead and copper in *mottramite* and *psittacinite*; as lead vanadate containing zinc and manganese in *déchenite*, *aroxène*, and *eusynchite*; as vanadate of lead and arsenic in *endlichite*; as bismuth vanadate in *pucherite*; as aluminium vanadate containing potassium silicate in *roscoelite*, and as vanadate of aluminium and calcium in *volborthite*. Vanadium is present in magnetites and most other iron ores, and becomes concentrated in the residues from their treatment, especially by the Thomas-Gilchrist process. It is said to be diffused with titanium, through all primitive granite rocks (Dieulafait), and has been found by Deville in *bauxite*, *rutile*, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands. Scacchi has observed its presence in incrustations on the Vesuvian lava of 1631, and Donath (D. P. J. 240, 318) has found as much as 0·16 p.c. of vanadic acid in a sample of commercial caustic soda.

On account of its intense affinity for oxygen at a red heat, vanadium is a most difficult metal to prepare in a state of purity. It can only be produced by heating the *anhydrous* dichloride in pure *dry* hydrogen (Roscoe).

Vanadium is a light, whitish-grey powder of a silver-white lustre under the microscope, stable in air, and having no action on water at ordinary temperatures, non-volatile and infusible in an atmosphere of hydrogen at a red heat. Its sp.gr. at 15° is 5·5. When heated rapidly in oxygen, or thrown in powder into a flame, it burns brilliantly.

Hydrochloric acid or aqueous alkalis are without action; hot concentrated sulphuric acid attacks it, and nitric acid, either dilute or strong, dissolves it rapidly; fused alkalis produce alkaline vanadates, with evolution of hydrogen. Vanadium combines directly with nitrogen when heated, forming the mononitride (Roscoe).

Vanadium belongs to the phosphorus group of elements. Like nitrogen, it forms five oxides: V_2O, V_2O_2, V_2O_3, V_2O_4, and V_2O_5. Hydrated oxides intermediate between the two latter have also been prepared (Brierley). The three first oxides act as bases, the two last as acids, forming hypovanadates and vanadates respectively.

Vanadium pentoxide. Vanadic acid V_2O_5 is the only oxide of industrial importance. It was prepared on the commercial scale in the form of ammonium metavanadate by Mr. Mellor, at Patricroft. The mineral employed was *mottramite* $(PbCu)_3(VO_4)_2 + 2PbCu(HO)_2$, which occurs in the copper-bearing Keuper beds at Alderley Edge and Mottram St. Andrew's, in Cheshire, as a film on the grains of sandstone. The sand is digested in concentrated hydrochloric acid, and the acid liquid is withdrawn. The solution, with the washings of the residue, is concentrated and evaporated with an excess of ammonium chloride, forming ammonium metavanadate, which, being insoluble in a concentrated solution of ammonium chloride, is precipitated. After being freed from copper and iron by repeated crystallisation, it is gently roasted in a porcelain vessel, with production of vanadium pentoxide. This is suspended in water and subjected to a current of ammonia gas, with formation of ammonium metavanadate, the solution being separated from the silica, phosphates, &c., which are not affected by ammonia, crystallised until free from phosphates, and gently ignited to produce pure vanadium pentoxide.

Vanadium pentoxide forms rhombic prisms, of a fine ruby-red colour by transmitted light, of sp.gr. 3·35, soluble in about 1,000 parts of water with formation of a yellowish solution which reddens litmus. At 658° (Carnelley) it fuses, forming a red liquid, which recrystallises in needles, with incandescence, on cooling. According to Ditte, this oxide exists in three modifications.

When heated in hydrogen it is reduced to the trioxide V_2O_3. When fused with sodium carbonate it forms sodium orthovanadate Na_3VO_4, but when heated with solution of the carbonate the metavanadate $NaVO_3$ is produced. In addition to meta-, ortho-, and pyro- vanadates corresponding to the phosphates, vanadium pentoxide forms tetra-, hexa-, and other more complicated vanadates.

This oxide combines with sulphuric acid, forming a compound $V_2O_53SO_3$. When the diluted solution of this salt is reduced by means of nascent hydrogen (by addition of zinc or sodium amalgam) it passes through various shades of colour, the original yellow solution of vanadic salt being reduced to the hypovanadous sulphate, producing first a green colour from the mixture of blue and yellow, next a blue, when the whole has been reduced to the hypovanadic condition, then green from the production of vanadous sulphate, and finally violet or lavender, when the hypovanadous salt is formed. The solution then forms a very powerful reducing agent, absorbing oxygen rapidly from the air, and acquiring a deep chocolate colour. It bleaches indigo and litmus as rapidly as chlorine.

Metavanadic acid HVO_3 may be prepared by boiling copper metavanadate with aqueous sulphurous acid. A mixture of brown and yellow crystals is first produced, the former being redissolved on continued boiling with excess of sulphurous acid. The remaining yellow crystals consist of metavanadic acid. The acid may also be prepared by addition of a solution of ammonium metavanadate to one of copper sulphate containing excess of ammonium chloride, until a permanent precipitate is produced, and heating for a few hours at 75°. The whole of the vanadium is slowly precipitated, the colour being finer when precipitation is slow (Gerland, B. 9, 874). Metavanadic acid forms brilliant golden or orange-coloured scales, which are used as a pigment in place of gold bronze under the name 'vanadium bronze.'

Ammonium metavanadate NH_4VO_3 is the most important of the vanadates. It is prepared by dissolving the pentoxide in ammonia.

According to G. Witz and F. Osmond (Bl. 38, 49; C. R. 95, 42), the slags produced while working the Thomas-Gilchrist process at the Creusot ironworks contain nearly 1·5 p.c. of vanadium, the quantity of that metal thus concentrated amounting to 60,000 kilos (nearly 59 tons) annually. They recommend the following process for the separation: 1 kilo of the roughly broken slag is treated with a quantity of hydrochloric acid insufficient to attack the whole (about 1 litre of acid at 21–22°Bé.) without stirring, 3 litres of water being added, and the whole remaining at rest for two days. The solution, having a sp.gr. of about 27°Bé. at 36°, is decanted and diluted to 15°Bé., and the silica is removed. The solution contains the vanadium in the hypovanadic condition, and may be used at once for the production of aniline black. If desired to produce hypovanadic phosphate, the solution is nearly neutralised and about 250 c.c. of saturated ammonium acetate solution is added. The bluish-grey precipitate produced, containing phosphates of iron, aluminium, and vanadium, is re-dissolved and again treated with ammonium acetate, the precipitate containing about 20 p.c. of vanadium.

If the slag contain less than 1·5 p.c. of vanadium, the hydrochloric acid solution is neutralised by the addition of a further quantity of finely-powdered slag. The solution becomes colourless, and a greyish granular precipitate separates, containing the whole of the vanadium and smaller proportions of the other less soluble phosphates. The precipitate is re-dissolved and re-precipitated as before. For the preparation of ammonium metavanadate, the phosphatic precipitate is roasted at incipient redness, and the ochreous-yellow mass of impure pentoxide is dissolved with the aid of ammonia, boiled until colourless and filtered, the ammonium vanadate being precipitated by the addition of excess of ammonium chloride (*v. Vanadium pentoxide*). From 4 kilos of slag containing 1·5 p.c. of vanadium, about 250 grms. of ammonium metavanadate may be produced. It is a colourless transparent salt, or white powder, difficultly soluble in water, insoluble in a concentrated solution of ammonium chloride and in ether. It is used, in conjunction with sodium chlorate, as an oxygen-carrier in the formation of the finest aniline black, only an extremely small quantity of the salt being required for a large amount of aniline (*v.* also CERIUM).

A very fine 'vanadium ink' is produced by the addition of gallic acid to a mixture of neutral ammonium metavanadate and gum water. This ink is not destroyed by acids, alkalis, or chlorine, but does not appear to be permanent. Soerensen (S. C. I. 1, 185) recommends the use of a solution of 1 lb. neutral ammonium metavanadate in 10 gallons of water for producing a permanent black dye on leather which has been tanned with nut galls.

Vanadium forms three chlorides: VCl_4, VCl_3, VCl_2, and four oxychlorides: $VOCl_3$, $VOCl_2$, $VOCl$, and V_2O_2Cl. A tribromide is known, but no fluoride or iodide has been prepared. H. Baker has prepared a series of crystalline hydrated fluoxyvanadates containing alkaline fluoride, vanadic anhydride, vanadyl fluoride, and water. Four sulphides are known: V_2S_2, V_2S_3, V_2S_4, and V_2S_5; the two latter act as acids, with formation of hypothiovanadates and thiovanadates respectively.

VANADIUM INK *v.* VANADIUM.

VANILLA (Span. *vainilla*, dim. of *vaina*, a pod), an aromatic substance employed to flavour chocolate and confectionery, and in the manufacture of liqueurs and perfumes, is the dried fermented pod of certain orchids belonging to the genus *Vanilla* found in Mexico, Columbia, Brazil, Peru, on the banks of the Orinoco, Parahyba, and other rivers in South America. The chief cultivated variety is *V. planifolia*, which is grown on a considerable scale in Mexico, Réunion, Mauritius, the Seychelles, and in Java. The long fleshy stem of the plant clings by its aerial rootlets to trees, and bears a greenish-white flower. The fruit is a pulpy pod, about 6 to 12 inches long and half an inch thick. In Mexico the plant is cultivated by planting cuttings at the feet of trees left in a clearing of the forest; these root in a few weeks and bear in the third year. In Réunion and in the Seychelles the plants are trained on trellis-work supported by trees, and are fertilised by hand. Care has to be taken to gather the pods at the proper time of maturity, as if over-ripe they split in drying, and if under-ripe they are deficient in flavour. In Mexico the gathered pods are allowed to lie in heaps until they begin to shrivel, after which they are heated, either by exposure to the sun or in ovens, when they gradually acquire a dark-brown colour. In Réunion the pods are immersed in boiling water for a few seconds, and then exposed to the sun for a few weeks in woollen cloths until they acquire the proper brown colour. As they become dry, they discharge a viscid liquid from the upper end, and are pressed from time to time to promote its flow. They are usually packed for the market in small bundles of fifty or one hundred in each.

The best vanilla is made in Mexico, which sends most of its produce to the United States. That from Réunion and Guadeloupe goes mainly to Bordeaux, that from the Seychelles to London, and that from Java to Holland.

The kind most esteemed in France is called *leq* vanilla; it is about 6 inches long and from $\frac{1}{4}$ to $\frac{1}{3}$ inch broad, narrowed at the two ends, curved at the base, somewhat soft and viscid, of a dark-reddish colour, and of a flavour of the Tonka bean. When it is covered with an efflorescence of *vanillin*, to which its characteristic fragrance is due, it is called *vanille givrée*.

The second sort, called *vanilla simarona*, is smaller in the pod than the preceding, not so brown in colour, and is free from efflorescence.

A third sort, which comes mainly from Brazil and Peru, is known as *vanillon*, and is the *vanilla pamprona* or *bova* of the Spaniards. The pod is comparatively broad and fleshy, and it contains a quantity of benzaldehyde which modifies the flavour. It is from 5 to 6 inches in length and $\frac{1}{2}$ to $\frac{3}{4}$ of an inch broad. It is soft, viscid, and of a strong but less agreeable smell than that of the *leq*.

The quantity of *vanillin* in the different varieties varies considerably. Mexican vanilla contains about 1·7 p.c., Réunion about 2 p.c., that from Java about 2·75 p.c., Rio vanilla about 1 p.c., whilst vanillon only contains from ·4 to ·7 p.c. All vanillas contain a small quantity of *vanillic acid* $C_6H_3(OH)(OCH_3)CO_2H$, which, however, is quite odourless.

Vanillin, the characteristic component of vanilla and the main ingredient of its crystalline coating, is the aldehyde of methyl protocatechuic acid $C_6H_3(OH)(OCH_3)CHO$ ($CHO:OCH_3:OH = 1:3:4$). It was formerly mistaken for benzoic or cinnamic acid. Afterwards it was regarded as coumarin, but was subsequently recognised by Gobley as distinct from that substance, and hence received its present name. Its formula was established by Carter (Bl. 17, 2), and its constitution by Tiemann and Haarmann, who prepared it artificially from *coniferin* $C_{16}H_{12}O_8$. This substance is contained in the cambium sap of various pines and firs, as *Abies excelsa*, *A. pectinata*, *Pinus Strobus*, *P. Cembra*, &c. On boiling this sap with water, and evaporating the clear liquid, freed from albumen, to about one-fifth its bulk, crystals of *coniferin* separate out, which on hydrolysis and on oxidation with chromic acid yield vanillin (Tiemann a. Haarmann, B. 8, 1118; 9, 1287). Vanillin is also obtained in a similar manner from *eugenol* $C_6H_3(OH)(OCH_3)CH=CH.CH_3$, a chief constituent of oil of cloves (*Eugenia Caryophyllata*) and of allspice (*Eugenia pimenta*).

Vanillin is also found in Siamese benzoin, in asafœtida, and, together with coniferin, in asparagus, and in the seeds of the lupine and of *Rosa canina*.

Vanillin forms white needles, possessing a strong taste and the characteristic smell of vanilla; m.p. 80–81°, b.p. 285° (without decomposition in a stream of carbon dioxide); soluble in 90–100 parts of water at 14°, and in 20 parts at 75–80°. Aqueous solution coloured violet by ferric chloride. Has an acid reaction and forms salts.

Artificial vanillin is made on an industrial scale in Germany. It can be obtained by replacing the nitro- group in *p*-nitro-*m*-methoxyl benzaldehyde by a hydroxyl group (Ulrich, B. 18, 2571; Germ. Pat. 18016; *v.* also L. Landsberg, Eng. Pat. 6190, 1886; Haarmann a. Reimer, Germ. Pat. 2792, 1883; D. P. J. [9] 253, 391).

VAREC. *Kelp v.* Iodine.

VARIOLARIN *v.* Lichens.

VARNISH. (Syn., *Vernis*, Fr.; *Lac*, *Firniss*, Ger.) A varnish may be described as a fluid of varying consistency, which when applied in a thin coat to the surface of a solid body dries eventually to a film of more or less hardness, lustre, and impermeability to air or moisture. It is obvious that the above definition embraces liquids of very varying composition, and the essential quality of a varnish—namely, that it will dry—is arrived at by the use of materials widely differing in their composition. The simplest form which a varnish can assume is that of a solution of a more or less elastic solid in a volatile menstruum, the drying of such a liquid, when spread out in a thin layer, being merely due to the evaporation of the solvent; to this class belong the great body of the spirit varnishes. When, however, in addition to the two kinds of substances mentioned above, a varnish contains some portion of oil, as in the case of the ordinary oil varnishes, the process of drying consists of two distinct operations, which take place side by side: the evaporation of the volatile solvent (if any be present), and the oxidation, or, in other words, the drying of the oil. The rapidity of the latter part of the process depends on the quality of the oil and on the amount and nature of the various metallic salts dissolved in the varnish; these, to a large extent, assist the oil to assimilate oxygen, and hence are termed driers.

Varnish is usually applied on a previously prepared surface by means of a brush in one or more coats. The spirit varnishes dry the most rapidly, but are more liable to be brittle and eventually to crack and peel off. This defect may be, to some extent, remedied by the addition of some elastic substance soluble in the spirit menstruum. Oil varnishes, however, are to a large extent free from this defect, the drying oil which they contain binding and softening the resin, and, although they take longer to dry, they are generally more lustrous and durable.

The solvents employed in making the various varnishes are chiefly alcohol, methylated spirits, naphtha, turpentine, and sometimes ether and chloroform. Of these, methylated spirits and turpentine are the more extensively used, and care should be taken that they are not adulterated.

Of oils, linseed oil is that in most general use; walnut and poppy oils are, however, sometimes employed. They should be carefully tested for their drying qualities and purity from foreign additions. Linseed oil as supplied by the crushers is generally tolerably pure, but sometimes samples are met with which contain resin or mineral oils, and give consequently a lower saponification equivalent. The best test, however, from a manufacturer's point of view, is the practical one—namely, that of making a small batch of varnish or drying oil with the sample.

The resins, or 'gums,' as they are technically termed, which enter into the composition of oil varnishes are chiefly animé, amber, copals of various kinds, and colophony or ordinary resin, while asphaltum or pitch is used for the darker sorts. The gums are washed and sifted, the better sorts being picked out by hand, and classified in various grades according to their colour and general soundness; and as the gum gives the hardening properties to the varnish, and is also the most expensive constituent, great care is exercised in its selection. Animé and amber give the hardest varnishes, and colophony the softest and most perishable.

In the manufacture of oil-varnishes the making-house plays an important part; it is here that the gum is melted or run, the oil heated, and the fusion of the two constituents takes place. As a good deal of inflammable vapour is given off during these operations, it is highly necessary that the building be so constructed as to rapidly carry away the vapours from contact with fire or a heated surface, and to this end the house should be lofty and well provided with chimneys possessing a good draught. In case of a pot suddenly catching fire, a sack is thrown over it and it is wheeled outside, cold oil being poured in to reduce the temperature if required.

Linseed oil, for the purpose of varnish making, is generally prepared or clarified in some manner before use, and in many cases the driers are added during this process. The oil is heated for two or three hours in a boiler at a gentle simmer, and then, after removing the scum, the driers are added according to the various receipts which the manufacturer prefers to employ; a very good one is to add for every 100 gals. of oil 14 lbs. of powdered litharge, the same quantity of red lead, and 7 lbs. of umber. The driers must have been previously heated in a stove, to expel all moisture. The heat is then continued for some two or three hours more, the whole being kept well stirred to prevent the driers sinking to the bottom; finally, the fire is withdrawn, and, after standing for two or three days to settle, the clear oil is decanted and tanked. If a drying oil be not required, calcined magnesia may be added instead of the above, and by operating in a similar way a so-called 'clarified' or 'prepared oil' is obtained.

In giving receipts for the preparation of oil or varnish, it is only intended to place before the reader a few of the typical ones which best exemplify the lines on which the manufacturer goes to work, as each different house has its own private receipts and methods of working, which for the most part are jealously guarded from the public eye, and are also capable of variation to almost any extent according to the requirements of the trade.

The first process in preparing an oil varnish is to melt or run the gum, and then to cause it to unite with the oil; to this end the gum is heated in a copper vessel over a rapid fire until it is perfectly liquid; the oil, which has been previously heated to 300°F., or thereabouts, is then cautiously added, and the whole is kept well stirred and the heating continued until the mixture is perfectly clear. If a drying oil has not been employed, the driers are now carefully sprinkled in, and the mixture further boiled, with continuous stirring, until a sample of it becomes stringy when cooled on a palette knife. The pot is then taken off the fire, and when cooled down sufficiently the turpentine is gradually added, stirring all the while, until the whole is thoroughly mixed. The varnish is then strained through a coarse sieve into a tank, where it remains until it is considered clear enough for use. The time required for this varies, and as all varnishes improve or ripen by age, the longer they are tanked the better. Old varnishes produce surfaces of much greater lustre than new ones, which are usually poor and dull.

It is generally considered that the good qualities of a varnish are largely dependent upon the efficient mixing of the gum and oil; if these are thoroughly incorporated the varnish will be freer from spots and blemishes on its surface, while if well boiled a varnish is said to flow more freely and to dry more rapidly. Excessive boiling, however, causes the varnish to require more turpentine for thinning, and the resulting fluid, being poorer in its non-volatile constituents, yields a thinner and less lustrous coat. No strict rule on this point can be given or adhered to, as some samples of oil or gum stouten more rapidly than others, and the final result has to be manipulated according to circumstances.

The drying of oil-varnishes varies considerably, according to their composition and the objects to which they have to be applied. Thus a good gold size will dry sometimes in a few minutes, while body or coach varnishes require twelve to twenty-four hours, and even then should be allowed two or three days to harden. On the other hand, polishing varnishes are generally dried by heat. Generally speaking, the more gum and driers a varnish contains the more quickly will it be transformed into a hard coat. As a varnish, however, is durable in proportion to its elasticity, it is not easy to prepare a varnish which shall be equally durable and hard-drying, and one or other of these qualities must be to some extent sacrificed in the final result.

Japanning is also a form of varnishing which requires for its completion the employment of heat; the original varnishes for lacquer work came from China and Japan, and are the resinous juices of trees belonging to the natural order *Anacardiaceæ*. They are purified and strained, being finally mixed with oil or colouring matter as required, and are dried by the aid of steam. Ordinary Japan is a black varnish made with asphaltum along with the other resins.

In the receipts given further on for the various kinds of varnish, it is to be noted that copperas and umber are not soluble in the menstruum, but only serve to harden and clarify; the various preparations of lead—such as red lead, litharge, and sugar of lead—dissolve, however, to a large extent, but an excessive quantity of driers is injurious to a varnish in many ways.

The manufacture of spirit varnishes is much less complicated than that of the oil preparations, as the former, in the general acceptation of the term, consist simply of various solutions of resins in spirituous media. The resins employed for this purpose are shellac in its various kinds. sandarac, gum benzoin, colophony, and some varieties of copal, and occasionally mastic and elemi. The solution of the resins is effected either cold or hot as circumstances require, heat presenting the advantages of rapid solution and clearing, while the palest varnishes are obtained by the cold process. Where heat is employed, preference is given to that of steam. A simple form of apparatus required for this process is furnished by a jacketed copper vessel, closed at the top, and connected with a condensing worm, motion being often communicated to its contents by a spindle fitted with blades at its lower end, and passing through the top by means of a stuffing-box. In this way the solution of the resin is rapidly effected, and the spirit which has distilled over during the operation may be returned at the close. When dissolved cold, the process is likewise facilitated by the employment of some convenient apparatus for keeping the gum in a continual state of agitation, and the caking together of the particles of gum is sometimes prevented by its previous admixture with a suitable quantity of sand or powdered glass. The varnishes are set aside in jars or other receptacles to settle, and are ready for use almost immediately. They dry very rapidly, and are, generally speaking, harder and more brittle than oil varnishes, and as their drying is merely dependent on the evaporation of the solvent, what are termed *driers* are not required.

Body varnish. Thoroughly melt 8 lbs. copal, and add 2 gals. pale drying linseed oil, previously heated to 300°; boil slowly till stringy, then take off the fire, and add 3 gals. of turpentine; strain, and allow to clear in the tank. This makes a good durable varnish. Animé is occasionally substituted for copal, the resulting varnish being harder; but amber gives a much darker result, and is oftener used on the Continent than in England.

Carriage varnish. Melt 8 lbs. copal, and add 2½ gals. hot oil; boil until stringy, then add ¼ lb. each of copperas and litharge or red lead; boil again, and thin with 5 or 6 gals. of turpentine. This receipt gives a good elastic varnish; if required harder, mix as required with an animé varnish made as above, substituting animé for copal. Cheaper qualities of body and carriage varnishes may be made by the employment in the above receipts of less gum and more driers, but the varnishes so obtained are, of course, less durable.

Oak varnish. Fuse 20 lbs. copal, and mix with 2 gals. hot drying oil; boil until it strings well, then add, when sufficiently cool, 5 gals. turpentine, and strain into tank. Cheaper qualities are obtained by the use of dark copal or colophony. This varnish is used for the inside fittings, doors, &c., of houses, and should dry hard in a few hours. Animé is sometimes used instead of copal for the best oak varnishes; also amber, where colour is not much considered.

Balloon or **flexible varnish.** This consists of a solution of indiarubber in chloroform, carbon bisulphide, or other light spirit, at the rate of 1 oz. to the pint. Or it may be prepared as an oil varnish by boiling, with constant stirring, 2 gals. of linseed oil with 6 oz. of copperas, the same weight of sugar of lead, and 1 lb. of litharge; boil until it strings well, and thin, if necessary, when cold with drying oil. Used for balloons, bags, and other purposes for which flexibility is an essential requirement.

Turpentine varnish. Dissolve, with or without the aid of heat, 6 lbs. colophony in 1 gal. turpentine. Makes a good and cheap varnish for wood or metal. Sometimes called wainscot varnish.

Patent leather varnishes. These are made from drying oil boiled with Prussian blue, and when cold ground with vegetable black, the quantities varying according to which coating is required. For the first coating 1 gal. of drying oil is boiled with 5 oz. pale Prussian blue to the right consistency, and afterwards ground with a little vegetable black. The last coat should have $\frac{1}{2}$ lb. pure Prussian blue and $\frac{1}{4}$ lb. vegetable black per gallon, while the intermediate coating varnishes are made in proportionate quantities. Each coat is stoved after application to the leather, and polished with pumice before the next coat is put on. The heat of the stove varies from 120–180°F., and the exposure of the skins from six to ten hours.

Black varnish, black japan, *&c.* Add to 16 lbs. of well-fused animé 1 gal. of hot drying oil, 3 lbs. dark resin, and 4 lbs. of asphaltum; boil well together, and thin with 2–3 gals. of hot turpentine. This makes the best coachmakers' japan.

A variety termed *ironwork black* may be prepared from 48 lbs. asphaltum, 10 gals. boiled oil, 7 lbs. each of red lead and litharge, and 3 lbs. white copperas; boil well for two hours, and thin with 25 gals. of turpentine. This is sometimes mixed with dark copal varnish to harden it.

Brunswick black is manufactured from 16 lbs. of asphaltum, melted and mixed with 1 gal. of dark drying oil, and finally thinned with 4 gals. of turpentine. Used to polish grates and ironwork.

Crystal or **paper varnish.** Use equal quantities of pale Canada balsam and spirits of turpentine. Chiefly employed for maps, prints, and paper articles. Or dissolve 3 ozs. of mastic in 1 pint of methylated spirit. For fixing pencil drawings.

Another varnish for paper may be made as follows:—Clear dammar resin is covered, in a flask, with $4\frac{1}{2}$ to 6 times its quantity of acetone, and allowed to stand for fourteen days at a moderate temperature, after which the clear solution is poured off. Three parts of this solution are then mixed with four parts of thick collodion, and the mixture allowed to become clear by standing. It is applied with a soft camel's-hair or beaver's-hair brush in vertical strokes. At first the coating looks like a thin white film, but on complete drying it becomes transparent and shining. It should be laid on two or three times. It retains its elasticity under all circumstances, and remains glossy in every kind of weather (S. C. I. 1882, 180).

A varnish which is said to coat the surface of the paper, and not permeate through it, has been patented. It is prepared by dissolving palmilate or oleate of alumina in some volatile spirit such as benzene or ether. After the evaporation of the solvent an impermeable varnish is left.

Spirit varnishes. For *brown hard* use sandarac 3 lbs., pale shellac 2 lbs., methylated spirit 2 gals.; dissolve, and add turpentine varnish 1 quart; agitate well, strain through gauze, and in a month decant the clear portion from the sediment. A cheaper varnish may be made from seedlac and yellow resin $1\frac{1}{2}$ lbs. each, methylated spirit 5 quarts, turpentine $1\frac{1}{4}$ pints; dissolve all together.

The best *white hard* is made from the following receipt:—Sandarac, 5 lbs.; camphor, 2 ozs.; pounded glass, 3 lbs.; methylated spirit, 7 quarts; dissolve, and when strained add 1 quart of pale Canada balsam.

A *soft brilliant* may be made from sandarac, 6 ozs.; elemi, 4 ozs.; animé, 1 oz.; camphor, $\frac{1}{2}$ oz.; methylated spirit, 1 quart; proceed as before.

Photographic varnishes. For dry plates, take of red shellac varnish, $\frac{1}{2}$ pint; methylated spirit, about $1\frac{1}{2}$ pints; add to or lessen spirit according to requirements. For wet-plate negatives, take $\frac{1}{2}$ pint white hard varnish, and add about 1 pint of methylated spirit, according as required.

Lac varnish. According to colour required, use pale or dark shellac, 8 ozs., and dissolve in 1 quart of methylated spirit. Or digest 5 ozs. shellac and 1 oz. borax in 1 pint of water at nearly the boiling heat till dissolved, then strain. When dry it is waterproof.

Coloured lac varnishes, or lacquers, may be prepared by adding to the spirit lac varnishes, as above, turmeric, gamboge, dragon's-blood, or other colouring matter soluble in spirit, according to the tint required. Applied to wood or metals to impart colour.

Mastic varnish. Pale gum mastic, 5 lbs.; coarsely-pounded glass, 3 lbs.; finest newly rectified oil of turpentine, 2 gals.; put in a four-gallon can, close down the bung securely, and keep rolling or in motion till all the gum is dissolved. This makes a very fine and pale varnish.

Label varnish. Sandarac, 53 parts; mastic, 20 parts; camphor, 1 part; oil of lavender, 8 parts; Venice turpentine, 4 parts; ether, 6 parts; alcohol or methylated spirit, 40 parts. Macerate for several weeks, agitating frequently until dissolved, and decant or strain from impurities. The varnish dries rapidly to a colourless, smooth, and glossy layer.

Wax varnish. Pure white wax, 1 lb.; melt with as little heat as possible; add of warm rectified spirit, sp.gr. ·830, 1 pint; mix perfectly, and pour out on to a cold porphyry slab; then grind with a muller to a smooth paste, adding more spirit as required; put the paste in a marble mortar, make it into an emulsion by gradually adding 3½ pints of water, and strain through muslin. Used as a varnish for paintings. When dry a hot iron is passed over it, or heat is otherwise evenly applied, so as to fuse it and render it transparent, after which, when cold, it is polished with a linen cloth.

For other receipts and information on the subject of drying oils and varnishes, see Cameron's Oils and Varnishes and Ure's Dictionary of Arts and Manufactures. J. K. C.

VARVICITE. *Hydrated manganese ore* $MnO_2.Mn_2O_3.H_2O$ (Rammelsberg), or

$MnO.3Mn_2O_3H_2O$

(Phillips) *v.* MANGANESE.

VASELINE. A yellowish semi-solid or viscous mixture of hydrocarbons, slightly fluorescent and odourless, made by purifying the residue left on distilling petroleum, or, artificially, by mixing solid and liquid paraffins until the required consistency is obtained.

American vaseline, made by the Chesebrough Company and other firms, is simply a vacuum residue (*v. American petroleum*, art. PETROLEUM) partially decolourised by treatment with animal charcoal. It is sold as melting either at 40° or at 51°. German vaseline (the *unguentum paraffini* of the German Pharmacopœia) is made by dissolving ceresin in paraffin-shale oil (*v.* Engler a. Böhn, D. P. J. 262, 468; Gerstenberger, S. C. I. 6, 676; Vulpius, S. C. I. 6, 719).

Vaseline is the *petrolatum* of the U.S. Pharmacopœia.

VAUQUELINITE. Native chromate of lead and copper.

VEGETABLE BUTTER *v.* BASSIA OILS; also OILS, FIXED, AND FATS.

VEGETABLE ETHIOPS. A form of charcoal obtained by the incineration of *Fuci*, *v.* IODINE.

VEGETABLE FATS *v.* OILS, FIXED, AND FATS.

VEGETABLE IVORY. The fruit of *Phytelephas macrocarpa* found in Columbia, South America.

VEGETABLE PARCHMENT *v. Parchment paper*, art. CELLULOSE.

VEGETABLE STEARIN *v.* STEARIN.

VEGETABLE TALLOW *v.* TALLOW.

VEGETABLE WAX (DETECTION OF, IN BEESWAX). The method recommended by a Commission of the German Society of Apothecaries (Ar. Ph. 24, 490) is to boil 1 grm. of the wax with 10 c.c. of water and 3 grms. of sodium carbonate for a quarter of an hour, and allow to cool, when the wax separates as a crust, and the underlying solution remains only slightly cloudy in the case of pure wax. But in presence of impurities an emulsion is formed beneath the crust of wax. The results of Röttger's experiments by this method show that 2 p.c. of Japan wax, stearic acid, or resin can be recognised in beeswax by the abnormal character of the emulsion formed, whilst in the case of an admixture of talc the test is less delicate, only 5 p.c. being recognisable (H. Röttger, Chem. Zeit. 14, 1473–1474; S. C. I. 1890, 83, 771; S. C. I. 10, 165); *v.* JAPAN WAX; also WAX.

VEGETO-ALKALOIDS. The vegetable alkaloids are nitrogenous carbon compounds possessing basic properties. They occur in plants, usually as the salts of organic acids. The greater number of them contain carbon, hydrogen, nitrogen, and oxygen, but in a few cases oxygen is absent (*e.g.* nicotine, conine). Chemically the vegetable alkaloids fall into three groups: (1) those which are derivatives of pyridine, *e.g.* atropine, conine; (2) those which are derivatives of quinoline, *e.g.* narcotine, cinchonine; and (3) those which are substituted amines and amides, and stand in a more or less simple relation to ammonia—*e.g.* choline, caffeine. Nearly all the vegetable alkaloids belong to the first and second groups.

The discovery of these bodies is due to the German pharmacist Sertürner, who, about the year 1807, isolated from opium a basic substance able to form salts, to which he gave the name 'morphium.' The principal physiological action of opium was found to be exerted by this substance, which has latterly been called morphia or morphine. The isolation, from other medicinal plants, of similar compounds capable of producing the physiological effect of the plants themselves quickly followed the discovery of morphine, and in the next few years strychnine and brucine were isolated from *Strychnos Nux-vomica*, and quinine and cinchonine from cinchona bark by Pelletier and Caventou. The first volatile alkaloid, conine, was obtained from hemlock in 1827 by Giesecke, and in the following year nicotine was described by Posselt and Riemann. At the present day a very large number of vegetable alkaloids are known, and the list is being extended every year. It has been agreed that the names of these compounds shall terminate in *-ine*.

Distribution and mode of formation.—The plants yielding alkaloids are widely distributed throughout the vegetable kingdom. It is remarkable, however, that so far alkaloids have been obtained from only one family of plants (*Colchiceæ*) belonging to the botanical division of monocotyledons, nearly all the alkaloids being found in dicotyledonous plants, although not in the families *Gramineæ* and *Labiatæ*; whilst alkaloids are very rarely found in plants belonging to the extensive natural order of *Compositæ*. The part played by alkaloids in the metabolism of plants is not well understood. The proportion of alkaloid generally reaches its maximum when the plant is mature. The alkaloid is distributed throughout the various organs, being found in the leaves, flowers, and seeds, as well as in the root and bark. When a plant dies down after flowering, the alkaloid accumulates in the root, whilst during the growth of a tree the alkaloids appear to be gradually deposited in the bark, and have therefore been compared to the excreta of animals. Very little is known as to the mode in which alkaloids are formed. It has been suggested that they may originate in the reaction of aldehydes with ammonia, it being known that certain aldehydes condense with ammonia to form pyridine derivatives. It is possible, however, that they may also result from the dehydration of the ammonium salts of organic acids. It is a significant fact that the ammonium salts of several of the acids which are found in plants in conjunction with alkaloids, such as meconic acid, chelidonic acid, and citric acid, may be converted, sometimes very readily, into derivatives of pyridine, a compound which is known to constitute the nucleus of a large number of the vegetable alkaloids. The experimental investigation of the natural mode of formation of alkaloids is beset with the great difficulty that the intermediate compounds, the precursors of alkaloids, are present only in minute quantity, and are hard to separate unchanged from the various plant constituents with which they are associated. Plants often contain several alkaloids, which, however, are generally found to be more or less closely related in their chemical structure.

Method of extraction.—Various processes are employed for the extraction of alkaloids from plants, the nature of the process depending partly on the properties of the alkaloid which has to be extracted, and partly on the nature of the other substances which occur with it in the plant. A method which succeeds in extracting the alkaloid from the root is not usually applicable without some modification for the extraction of the alkaloids from the leaves even of the same plant, owing to the fact that the root and leaves contain different constituents.

It will only be possible within the limits of this article to allude to the general method of procedure. In the older processes the finely powdered part of the plant (root, bark, &c.) is exhausted by percolating it with a dilute mineral acid, which decomposed the natural organic salt of the alkaloid, forming a hydrochloride or sulphate readily soluble in water. The alkaloid is precipitated on the addition of an alkali to this solution; or the plant is incorporated with lime and water to liberate the alkaloid, and the dried mass exhausted with a suitable solvent, generally with alcohol. In some cases the alkaloidal salts have been extracted direct from the plant by means of dilute alcohol, and the alkaloid precipitated by an alkali after the alcohol has been distilled off. For the removal of colouring matter &c. from the alkaloidal solutions, precipitation with lead acetate has been largely resorted to, the precipitate containing the lead salts of tannic and other organic acids as well as the colouring matter. Animal charcoal has been extensively employed for separating the last traces of colour from the alkaloid or its salt, the alkaloid being finally crystallised from alcohol or water.

The methods at present used do not differ essentially from those above described. Now that it is known how readily some alkaloids are hydrolysed and otherwise altered by strong acids and alkalis, the use of mineral acid, except in very dilute solutions, has been abandoned; tartaric or acetic acid being employed instead for purposes of extraction. Ammonia or an alkali bicarbonate is to be recommended for precipitating alkaloids in the place of potash or soda. The use of animal charcoal for decolourising alkaloidal solutions requires caution, since some alkaloids are retained by this substance, more especially when they are in the free state.

In the majority of cases the following method, modified where necessary, will be found useful for extracting alkaloids from plants. The finely-powdered material is mixed with about one-tenth of its weight of lime, and made into a paste with water. When an alkaloid is decomposed by lime, magnesia may be substituted for it. The mixture, which now contains the free alkaloid, is thoroughly dried in a water-oven and powdered. It is then packed in an extraction apparatus (*v.* EXTRACTION APPARATUS) and exhausted with an appropriate solvent, chloroform, ether, alcohol, 'heavy' or 'light' petroleum, or rectified fusel oil, the last two liquids being extensively employed on the manufacturing scale. By this means the alkaloid is extracted, together with very little colouring matter. The solvent is distilled from the solution, and the residue mixed with a dilute acid, when the alkaloidal salt dissolves, leaving the fat, resin, &c. The alkaloid is obtained by precipitating this solution with a slight excess of ammonia. When the solvent used for the initial extraction is only slightly soluble in water—*e.g.* chloroform or petroleum—the separation of the alkaloid from the fat, resin, and colouring matter may be effected by thoroughly agitating the liquid with acidulated water. The aqueous layer now contains the alkaloidal salt, whilst nearly the whole of the impurities remain in the organic solvent. Similarly, instead of precipitating the acid liquid with alkali, it may be mixed with chloroform or petroleum, then made alkaline and thoroughly agitated; the liberated alkaloid now dissolves in the organic solvent, and may be obtained from it by evaporation. These modifications are particularly useful on the small scale, and are widely resorted to in toxicology, since nearly the whole of the alkaloid may be recovered in this way, whereas when the alkaloid is obtained by precipitation, some is liable to be lost through solubility. When it is not easy to obtain a colourless alkaloid by crystallisation from alcohol or ether, it should be converted into a salt, and repeatedly crystallised from water or alcohol until a colourless salt is obtained, from which the alkaloid may be regenerated.

When the alkaloid is volatile, the parts of the plant are distilled with very dilute alkali; the liberated alkaloid condenses with the steam, and may be extracted with a suitable solvent from the aqueous distillate.

Further information respecting the extraction of alkaloids from plants will be given in connection with the account of each alkaloid (*v. infra*). The worker should also consult the original memoirs there referred to, and also Dragendorff's Plant Analysis (English translation by H. G. Greenish); Allen's Commercial Organic Analysis, vol. iii.

Purification and separation of alkaloids.—An alkaloid having been isolated in a pure state (*i.e.* free from non-alkaloidal substances), it is necessary to obtain evidence of its being a single body before its composition and properties are investigated. This may be done by crystallising the alkaloid or one of its salts in several fractions, the properties of each fraction being examined; they should, of course, be identical if the alkaloid is homogeneous. The melting-point is often conveniently made use of for this purpose, or, when this is not sharply defined, some other physical property—*e.g.* rotatory power, solubility, &c.

In those cases where a distinctive physical property cannot be found, combustions must be made of the different fractions in order to determine whether their composition is identical. The aurichlorides have frequently proved to be very useful as a means of characterising and purifying alkaloids, since these compounds, as a rule, are easily prepared, crystallise well, and melt sharply, each at a different temperature, even when the alkaloids themselves are closely related. An aurichloride having been obtained of constant melting-point—*i.e.* not changed by recrystallisation—the corresponding alkaloid may be regenerated from it by precipitating the gold from it, suspended or dissolved in water with the slightest possible excess of hydrogen sulphide, filtering, and expelling any trace of hydrogen sulphide, and then recovering the alkaloid from the solution of the hydrochloride in the usual manner. For further information concerning the methods of separating and characterising alkaloids, see Ladenburg on the alkaloids of *Duboisia*, *Hyoscyamus*, and *Belladonna* (B. 13, 257, 909, 1549 *et seq.*); Wright and Luff on the aconite alkaloids (C. J. 33, 151, 318; 35, 387); Dunstan and Chaston on the alkaloids of *Scopola carniolica* (Ph. [3] 20, 461), Dunstan and Ince; Dunstan and Umney on the alkaloids of *Aconitum Napellus* (C. J. 59, 271; 61, 385).

The homogeneity, exact composition, and the characteristic physical and chemical properties of many of the alkaloids are still undetermined. Unfortunately, it is the practice of many of those who examine the alkaloidal constituents of plants to content themselves with isolating, in a more or less pure state, the chief alkaloid, and giving a name to it without examining its physical and chemical properties or those of its salts, so that no means exist by which it can be characterised with certainty. The so-called colour reactions are as a rule valueless for this purpose. Much useful work remains to be done in preparing a number of the vegetable alkaloids perfectly pure, and then examining their principal properties. Until this preliminary work has been done, inquiries into the chemical nature of these bodies are impossible, whilst an examination of the physiological action is of very doubtful value.

Physical and chemical characters and constitution of the vegetable alkaloids. Most of the vegetable alkaloids are solid substances, many of them being crystalline. A smaller number are liquid (conine, nicotine, pilocarpine, &c.); some of these, being volatile, distil with water, although alone they boil at much higher temperatures, often without appreciable decomposition. The crystalline alkaloids generally melt sharply at definite temperatures, and the observation of the melting-point of an alkaloid, or of one of its crystalline compounds, is a trustworthy means, not only of identifying it, but also of ascertaining its purity, since small quantities of impurity considerably lower the melting-point. The volatile alkaloids may be identified by their boiling-points.

Most of the vegetable alkaloids are optically active, *i.e.* rotate the ray of polarised light. The greater number are lævorotatory. A few are dextrorotatory, notably aconitine, pilocarpine, and narcotine. A few of the alkaloids are optically inactive—*e.g.* piperine, berberine, and cryptopine. The alkaloidal salts generally exhibit the same kind of optical activity as the alkaloids themselves; dextrorotatory alkaloids furnish dextrorotatory salts, lævorotatory alkaloids lævorotatory salts. The salts of the lævorotatory nicotine and narcotine are, however, dextrorotatory, whilst the dextrorotatory aconitine furnishes a lævorotatory hydrobromide.

The majority of the vegetable alkaloids are insoluble, or very sparingly soluble, in water; their best solvent is alcohol. Usually they are also dissolved by chloroform, ether, benzene, and amyl alcohol, sometimes by light petroleum. Their aqueous solutions are frequently strongly alkaline to litmus, and precipitate hydroxides from solutions of metallic salts.

Like ammonia, the vegetable alkaloids combine directly with acids to form salts, which are usually crystalline, and often soluble in water but generally insoluble in chloroform and ether.

In their combinations with acids the alkaloids nearly always act as mon-acidic bases, even when they contain two atoms of nitrogen in the molecule, that is to say, they unite in only one proportion with acids to form stable salts. To this rule, however, notable exceptions exist, especially among the cinchona alkaloids; *e.g.* quinine is a diacidic base.[1]

The ordinary salts will be alluded to later in connection with the particular alkaloids. Attention will be directed here to certain alkaloidal compounds, which are important in connection with the detection and identification of the vegetable alkaloids.

Auric chloride ($AuCl_3$) combines with the hydrochlorides of the alkaloids, forming well-defined *aurichlorides*,[2] usually composed of one molecule of the alkaloidal hydrochloride and one molecule of auric chloride ($B.HCl.AuCl_3$). These compounds are frequently sparingly soluble in water, and are thrown down as pale-yellow precipitates when an aqueous solution of auric chloride is mixed with an aqueous solution of the alkaloidal hydrochloride. Sometimes, however, the aurichlorides are soluble in water. They may be crystallised from their solutions in alcohol or water acidulated with hydrochloric acid. As has been already pointed out, these crystalline compounds melt sharply and are used in characterising alkaloids. They are also conveniently employed in ascertaining the formula-weights of the alkaloids, the gold being determined by ignition. In cases where neither the alkaloid nor one of its ordinary salts can be crystallised, or readily obtained pure, the percentage composition of the alkaloid may be arrived at from the results of the combustion of the pure aurichloride. When only small quantities of material are available, it is important to be able to determine the composition of the aurichloride without losing the alkaloid, which, of course, is inevitable if the gold is determined by ignition in the usual manner. The following process renders it possible to estimate and recover the alkaloid and also to estimate the gold and the chlorine in one and the same quantity of aurichloride. A weighed quantity of the aurichloride (·5-1 grm.) is dissolved or finely suspended in water, and decomposed by the gradual addition of a very slight excess of aqueous hydrogen sulphide; the resulting precipitate of gold sulphide is washed, dried, ignited, and the residue of gold weighed. The filtrate and washings are made alkaline with ammonia, and the alkaloid extracted by agitation with chloroform or ether; the residue of alkaloid left on the evaporation of the solvent is dried and weighed. The alkaline aqueous solution is now strongly acidified with nitric acid, and the chlorine precipitated with silver nitrate in the ordinary manner.

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[1] The nomenclature of alkaloidal salts is in a very unsatisfactory state. They were originally named after the similar compounds of ammonia, viz. hydrochlorate, sulphate, nitrate, &c. These names have long ceased to be used for the ammonia compounds, which are now regarded as salts of 'ammonium'—viz. ammonium chloride, ammonium sulphate, &c. No analogous change has, however, been made in the names of alkaloidal salts, the salts of morphine, for example, being still called morphine hydrochlorate (or hydrochloride), morphine sulphate, &c., and not morphium chloride, morphium sulphate, &c. The only change that has been made is to alter 'hydrochlorate,' not into 'chloride,' but into 'hydrochloride,' which has the advantage of indicating that the compound contains the entire molecule of hydrochloric acid, and in this respect differs from the metallic chlorides. This reform has been extended to the 'hydriodates' and 'hydrobromates,' which are now called 'hydriodides' and 'hydrobromides.' It has not, however, been applied to the other salts (sulphate, nitrate, &c.), which, though similarly constituted, are not termed 'hydrosulphates,' 'hydronitrates,' &c.

[2] Compounds of the alkaloidal hydrochlorides with auric chloride will be called *auri-chlorides*, the corresponding compounds with platinum chloride, *platini-chlorides*, with mercuric chloride *mercuri-chlorides*.

A compound of the alkaloid itself with auric chloride will be termed an *auric chloride compound*, or simply (for example) pilocarpine auric chloride, and the similar *mercuric chloride compound*, pilocarpine mercuric chloride.

Auric chloride also appears to combine with the alkaloids themselves, as well as with their hydrochlorides, forming auric chloride compounds ($\bar{B}.AuCl_3$), which are stable crystalline salts composed of one molecule of the alkaloid and one of auric chloride. They are obtained by mixing together alcoholic solutions of the alkaloids and auric chloride. The determination of the melting-point and composition of these compounds furnishes an additional means of characterising certain alkaloids. So far these compounds have only been prepared from a few alkaloids (Dunstan a. Ince, C. J. 59, 271; Hardy a. Calmels, Bl. 48, 220), but there is reason to believe that they are obtainable from many of the vegetable alkaloids.

Aurochlor derivatives of caffeine and isaconitine have recently been obtained. They are produced from the aurichlorides by the loss of two mol. props. of hydrogen chloride, and may therefore be regarded as derived from the alkaloid by the replacement of one atom of hydrogen by the group $AuCl_2$ (Dunstan a. Shepheard, C. J. 63, 201; Dunstan a. Harrison, C. J. 63).

Platinic chloride combines with alkaloidal hydrochlorides to form platinichlorides ($\bar{B}.HCl.PtCl_4$), which are sometimes precipitated when aqueous solutions of those substances are mixed, but are generally more soluble than the corresponding aurichlorides. They frequently crystallise well, and are useful in determining the formula-weights of the alkaloids, the platinum being estimated by carefully igniting the salts and weighing the metallic residue.

Palladium chloride and **mercuric chloride** also form double salts with certain alkaloids.

Picric acid precipitates the solutions of most alkaloidal salts, and the yellow picrates may often be crystallised; in very acid or dilute solutions the precipitation of the picrate is frequently not observed. The alkaloids may be recovered from the picrates by decomposing them with aqueous alkali, and extracting the liquid with ether or chloroform.

Tannic acid also precipitates solutions of many alkaloidal salts.

Iodine dissolved in aqueous potassium iodide precipitates the solutions of most alkaloidal salts. The precipitate is reddish-brown when the solution is dilute, but in strong solutions this precipitate at once aggregates to a greenish-black mass. The precipitates consist of the periodides of the alkaloids ($\bar{B}.HI.I_2$ or I_4). Many of them crystallise well from alcoholic solution, the crystals being green by reflected and red by transmitted light. The alkaloid may be recovered from these periodides most safely by dissolving the compound in aqueous sodium thiosulphate, then adding excess of ammonia, and shaking out the alkaloid with ether or chloroform (Dunstan a. Ransom, Ph. [3] 14, 623).

Mercuric iodide dissolved in aqueous potassium iodide (Mayer's solution) produces an abundant yellowish-white flocculent precipitate of indefinite composition in solutions of nearly all alkaloidal salts, and for this reason is one of the best general reagents for detecting alkaloids (Mayer, Vierteljährschrift für Pharm. 13, 43; Baur, Ar. Ph. [3] 5, 214, 289). The precipitation of an alkaloid by this reagent is often quite complete if certain precautions are taken, the character of which varies with different alkaloids, some being completely precipitated only when the alkaloidal solution is neutral, others requiring that the solution shall be faintly acid to complete the precipitation, while a few alkaloids are only precipitated by this reagent from a strongly acid solution. Although the precipitates (double iodides of mercury and alkaloids) produced by this reagent have not a constant composition, yet the quantity of a known alkaloid contained in a given solution may be volumetrically estimated by its means, the precipitatory power of a cubic centimetre of the solution having been previously found for the alkaloid in question (*v. Detection and estimation of alkaloids*). The alkaloids may be recovered from these precipitates by suspending them in water, and passing hydrogen sulphide through the mixture. After filtering off the mercuric sulphide, a solution of the alkaloidal hydriodide is obtained, from which the alkaloid may be liberated and extracted in the usual way. Or the precipitate produced by Mayer's reagent may be decomposed with stannous chloride, and the alkaloid liberated from the solution by potash.

Bismuth iodide or cadmium iodide dissolved in aqueous potassium iodide also precipitates alkaloids, the character of the precipitates being similar to those produced by Mayer's reagent.

Phospho-molybdic acid, prepared by adding excess of nitric acid to the solution of the sodium salt, produces a white precipitate in the solutions of most alkaloidal salts (Sonnenschein, A. 104, 45).

Phospho-tungstic acid acts similarly. Alkalis liberate the alkaloids from these precipitates.

Of the very numerous reactions of the vegetable alkaloids the following are some of the most important in relation to the chemical constitution of these bodies.

In their behaviour towards alkyl iodides (methyl iodide) most of the alkaloids act as tertiary bases; a few, including conine, are secondary compounds. An examination of the properties and modes of decomposition of the 'ammonium iodides' formed by the combination of alkaloids with alkyl iodides has sometimes thrown important light on the constitution of the alkaloids.

The nitrogen, which may be regarded as the centre of force, chemical and physiological, is not easily separated from the vegetable alkaloids. In a few instances ammonia or an amine is formed by reduction with concentrated hydriodic acid, or by the action of concentrated aqueous alkali. Sometimes fusion with alkali, or distillation over hot soda lime, will lead to the elimination of the whole or a part of the nitrogen in the form of ammonia or an amine, but in the majority of cases under such treatment a pyridine or quinoline derivative is obtained—that is to say, the nitrogen is not separated from the closed chain which constitutes the nucleus of the molecule. Conine yields ammonia when it is heated with concentrated hydriodic acid, whilst morphine, tropine, and ecgonine afford methylamine when acted on by alkali, proving that the methyl group in these compounds is linked to nitrogen. On the other hand, nicotine, pilocarpine, and many other alkaloids furnish pyridine derivatives when similarly acted on. Cinchonine, papaverine, strychnine, and berberine under the same treatment yield derivatives of quinoline.

The less energetic action of alkalis (baryta) and of mineral acids effects the hydrolysis of certain alkaloids, the products being usually a non-nitrogenous acid and a nitrogenous base. By the reaction of this acid and base, the natural alkaloid is often reproduced. Thus atropine suffers hydrolysis, producing the base tropine together with tropic acid

$$C_{17}H_{23}NO_3 + H_2O = \underset{\text{(tropine)}}{C_8H_{15}NO} + \underset{\text{(tropic acid)}}{C_9H_{10}O_3}$$

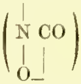
and by heating these substances together the reaction may be reversed, and atropine (tropyl tropine) re-formed. Similarly, piperine may be resolved into piperidine and piperic acid, aconitine into aconine and benzoic acid.

Oxidising agents, especially permanganate or chromic acid, convert many vegetable alkaloids into acids belonging to the pyridine and quinoline series, and these are sometimes accompanied by paraffinic acids resulting from the oxidation of side chains attached in the alkaloidal molecule to the nucleus of pyridine or quinoline. Thus nicotine on oxidation furnishes nicotinic or pyridine-carboxylic acid, which yields pyridine itself when distilled with lime, whilst conine affords, besides a similar pyridinic acid, the normal butyric acid.

Reducing agents attack most alkaloids, and as they are generally unsaturated compounds hydrogen is often taken up (from sodium amalgam and water), forming hydrides of the original compounds. Thus cinchonine combines with two atoms of hydrogen, forming the so-called dihydrocinchonine, or more properly cinchonine dihydride; berberine and papaverine combine with four atoms of hydrogen, producing tetrahydrides, whilst nicotine unites with six atoms of hydrogen, furnishing a hexahydride. When the deoxidation of alkaloids is effected by means of red-hot zinc-dust, pyridine and quinoline derivatives are frequently obtained. The halogens react with nearly all alkaloids, forming additive compounds, as well as haloid derivatives.

The action of phosphoric chloride or oxychloride—or better, because less violent, that of acetic or benzoic chloride (or anhydride)—throws light on the important question as to the mode of the union of the oxygen which nearly all the alkaloids contain. In many cases the presence of one or more hydroxyl (OH) groups has been established. Atropine and conydrine contain one hydroxyl group, whilst morphine contains two. Many of those alkaloids which contain hydroxyl are converted by the action of dilute mineral acids, or of strong aqueous tartaric acid, into bases which differ from them by the absence of the elements of a molecule of water. These compounds, which closely resemble the parent alkaloids, are termed 'apo-' or better 'anhydro-' compounds; thus atropine yields anhydro-atropine, morphine 'apo-' or anhydro-morphine, aconitine anhydro-aconitine.

Certain alkaloids contain one or more methoxyl (OCH_3) groups, the presence of which is ascertained by heating with concentrated hydriodic acid, when methyl iodide is formed. The quantity of iodide formed may be estimated (Zeisel, M. 6, 989; Benedikt a. Grüssner, Chem. Zeit. 13, 872), and from this result the number of methoxyl groups present may be calculated. Quinine and quinidine contain one methoxyl group, thebaine and apparently brucine contain two, whilst narcotine contains three, and papaverine four.

In many alkaloids one or more atoms of oxygen are present in a form other than hydroxyl or methoxyl. Besides carbonyl (CO), which is a frequent constituent, the existence of a betaïne group  $\left(\begin{array}{cc} | & \\ \mathrm{N} & \mathrm{CO} \\ | & | \\ \mathrm{O} & \rfloor \end{array}\right)$ has been demonstrated in trigonelline and in pilocarpine.

The chemical behaviour of the vegetable alkaloids shows them to be, with but few exceptions, derivatives of pyridine (*e.g.* conine and atropine) and quinoline (*e.g.* cinchonine, papaverine). On this account Königs (Studien über d. Alkaloide, Munich, 1880) has proposed to designate vegetable alkaloids only those substances which are so derived, such bodies as caffeine, theobromine, muscarine, and choline, which are not pyridine or quinoline derivatives, being called vegetable bases. The precise constitution of a few alkaloids has been more or less completely established, and their syntheses have been either partially or entirely effected; *e.g.* conine, the principal alkaloid of hemlock, has been proved to be α-propyl-hexahydropyridine; piperine, the alkaloid of pepper, the piperyl derivative of hexahydropyridine; pilocarpine, the alkaloid of jaborandi, the betaïne of a substituted pyridine-lactic acid (pilocarpic acid); atropine, the alkaloid of belladonna, the tropyl derivative of hydroxyethyl-methyl-tetrahydropyridine; trigonelline, the methyl betaïne of β-pyridine-carboxylic acid, &c., &c.

Comparatively little work remains to be done in order to completely establish the chemical constitution of a number of alkaloids other than those mentioned above, and the reactions of so many of these bodies have been carefully investigated in recent years that chemists are now quite familiar with the characteristic features of the structure of these bodies. For further information regarding the constitution of the vegetable alkaloids *v.* Königs, Studien über d. Alkaloide, Munich, 1880; Pictet, Les Alcaloïdes Vegétaux, Paris, 1888, and especially the original memoirs referred to in connection with each alkaloid.

Detection and estimation of alkaloids.—The presence of an alkaloid may be detected by the use of the general reagents referred to above, which, as a rule, afford most delicate indications when added to a slightly acidified solution. The evidence thus obtained must be confirmed by an examination of the chief chemical properties of the substance. Many of the alkaloids give characteristic colour reactions when mixed with sulphuric acid and other reagents; these will be alluded to later in connection with each alkaloid. It should, however, be remembered that, with possibly one or two exceptions, colour reactions cannot be relied on as conclusive proof of the presence of a particular alkaloid, since very similar colour reactions are often given by more than one alkaloid, and on the other hand distinctive colours are frequently obscured by the presence of impurity.

For the detection and separation of alkaloids in toxicology special processes are used, which in principle are the same as those employed to extract alkaloids from plants, but are longer, and differ somewhat in the mode of procedure. The methods devised by Stas-Otto, by Dragendorff, and by Erdmann and Uslar are those usually resorted to. For details of these methods the following works should be consulted: Husemann, Toxicologie; Dragendorff, Gerichtlich-Chemische Ermittelung von Giften; Taylor's Toxicology, edited by Stevenson; Wynter Blyth, Poisons; Allen's Commercial Organic Analysis, vol. iii.; WATTS' DICTIONARY OF CHEMISTRY, new edition, art. ALKALOIDS.

For the estimation of alkaloids it has been proposed to use a standard Mayer's solution volumetrically, with as pure a solution of the alkaloidal salt as possible. The titration is conducted in the usual way, the end of the precipitation being looked for. Since the precipitate produced by this solution has not the same composition with different alkaloids, the Mayer's solution is empirically standardised, the value of a cubic centimetre being separately found by actual trial with each alkaloid. For a list of these values *v.* Dragendorff's Plant Analysis. The method is trustworthy when it is known that only one alkaloid is contained in the solution, and when the titration is conducted under precisely the same conditions as those which were observed in standardising the Mayer's solution with the particular alkaloid which is being estimated. Whenever possible, the quantity of alkaloid contained in a given material should be determined by isolating it pure, and weighing it as such, or as a salt.

For the estimation of alkaloids in plants and in medicinal preparations (tinctures, extracts, &c.) made from them, processes very similar to those described for the extraction of alkaloids from plants are used quantitatively with certain precautions, the residue of alkaloid being finally weighed. The details of these processes differ with each plant and its preparations. The more important methods will be alluded to in connection with the various alkaloids. For further information on the subject *v.* Dragendorff, Der Chemische Werthbestimmung die Starkwirkenden Droguen; Prescott, Organic Analysis, and various papers in the 'Pharmaceutical Journal' (1879-93).

It will not be possible within the limits of this monograph to give an account of every known vegetable alkaloid, but only to allude to most of those which are of practical importance in some connection or another, because they are manufactured on a large scale, or are used largely in medicine, or on account of the familiarity of the plants which yield them, &c. Even in these cases it will be impossible to do much more than afford an outline of the principal properties, reactions, modes of preparation, detection, and estimation of each alkaloid. Processes for the extraction, detection, and estimation of important alkaloids as a rule will be somewhat fully described, whilst questions relating to their chemical constitution, although not exhaustively discussed, will, in important instances, be dealt with sufficiently to make clear the character of the evidence that has been utilised in effecting the remarkable progress of the last twenty years. References will be given to the original memoirs from which fuller information may be obtained. In general, more detailed information respecting the properties and reactions of alkaloids and their salts will be found under the separate headings in WATTS' DICTIONARY OF CHEMISTRY, by Muir and Morley.

Since it is not possible at the present time to adopt a chemical classification of the vegetable alkaloids, and as a system of classification founded on that of the plants which yield them would be without significance in a chemical dictionary, the principal alkaloids will be considered in alphabetical order, except in cases where several alkaloids are furnished by one plant, when these will, as a rule, be considered in connection with the principal alkaloid.

Aconitine and the **Aconite alkaloids.** Our knowledge of the aconite alkaloids is at present in a very unsatisfactory state. Owing to the great difficulty of extracting them without change from the plants, and of obtaining them in a perfectly pure state, conflicting accounts of their composition and properties have been given by different observers. The following list includes the alkaloids about whose existence in the principal species of aconite there seems to be little or no doubt:—

In *Aconitum Napellus* .	Aconitine Isaconitine Homisaconitine Aconine

In *Aconitum ferox* . .	Pseudaconitine Amorphous bases
In *Aconitum japonicum* . (Japanese aconite)	Japaconitine Amorphous bases
In *Aconitum lycoctonum* .	Lycaconitine Myoctonine

It is certain that the various aconite alkaloids are closely related to each other and that their chemical structure is similar, but the relationship subsisting between most of them has not yet been made out, whilst virtually nothing is known as to their chemical constitution. It will not be possible to trace their structural connection until a great deal of preliminary work has been done in obtaining each alkaloid perfectly pure, characterising it by a careful study of its physical and chemical properties, and establishing precisely wherein it differs from the other alkaloids of this group.

Our knowledge of the pure alkaloids being in this imperfect state, it is scarcely necessary to point out that very little accurate knowledge has been gained with reference to the remarkable physiological activity of the chief of these alkaloids (aconitine), which must be reckoned among the most powerful poisons at present known. The many results which have been recorded must be accepted only as defining in a broad and general manner the kind of physiological effect which these alkaloids produce, since it is well known that few, if any, experiments have been made with material of demonstrated purity.

Aconitine $C_{33}H_{45}NO_{12}$ or $C_{33}H_{43}NO_{12}$, the principal alkaloid contained in *Aconitum Napellus*, or monkshood, which also contains the alkaloids isaconitine, homisaconitine, and aconine, apparently in combination with aconitic acid. Aconitine was discovered in 1833 by Geiger and Hesse (A. 7, 276), and first crystallised by T. B. Groves in 1860 (Ph. [2] 8, 121). Its chemical properties were investigated by Wright and Luff (C. J. 31, 143, 33, 151, 318 *et seq.*), and later by Dunstan and Ince (*ibid.* 59, 271), Dunstan and Umney and Dunstan and Passmore (*ibid.* 61, 385, 395).

Preparation.—The finely powdered root is extracted with alcohol acidified with tartaric acid. Mineral acids must not be employed, since they readily hydrolyse aconitine. The alcoholic solution is evaporated at a low temperature (60°), water is added to the residue, and the resin &c. removed by agitation with light petroleum. The aqueous liquid is now precipitated with an alkali carbonate. The precipitate of alkaloid is extracted with ether, and the ethereal solution shaken with aqueous tartaric acid. By this means a small quantity of resin is left dissolved in the ether. The alkaloid is now again precipitated from the acid solution and crystallised from ether, the crystallisation being assisted by the cautious addition of light petroleum to the ethereal solution. Finally, the alkaloid is purified by converting it into the hydrobromide, and repeatedly crystallising this salt from water. The alkaloid is then regenerated from the pure salt (Duquesnel, A. Ch. [4] 25, 151; Wright, C. J. 31, 143).

The following process has given good results, both on the small and large scale (Dunstan a. Umney, C. J. 61, 385):—

The finely powdered root is exhausted with amyl alcohol (b.p. 120–130°). The solution is agitated with dilute (1 p.c.) sulphuric acid, and the acid solution twice extracted with a small quantity of chloroform in order to remove dissolved amyl alcohol. The liquid is now exactly neutralised with dilute ammonia, and gently warmed to expel the dissolved chloroform. To the cold solution a slight excess of ammonia is added, and the liquid repeatedly extracted with ether until nothing is removed. The aconine remains dissolved in the water, the aconitine with some isaconitine and homisaconitine passing into the ether. The ethereal solution is washed with a small quantity of water and evaporated. The residue is converted into hydrobromide by dissolving it in dilute hydrobromic acid, care being taken to avoid excess of acid. The exactly neutral liquid is evaporated to a small volume and allowed to crystallise. The crystals of aconitine hydrobromide are separated from the liquid, from which a further supply of crystals may be obtained; even when the mother-liquid is syrupy, crystals will form, especially if a small crystal of aconitine hydrobromide is introduced into it. The aconitine hydrobromide is recrystallised several times from water until it melts at the proper temperature, and then is converted into the alkaloid by the addition of a slight excess of ammonia to its aqueous solution, the alkaloid being extracted by ether in the usual way. The washed ethereal solution is thoroughly dried by agitation with fused calcium chloride and evaporated. The small crystals which are deposited as the ether evaporates may be recrystallised from a mixture of alcohol and ether, by which means large crystals may be readily procured.

The root of *A. Napellus* appears to contain from ·02–·04 per cent. of aconitine.

Properties.—Colourless anhydrous tabular prisms, belonging to the rhombic system. For a description of its crystallographic characters, see Tutton (C. J. 59, 288). Easily soluble in chloroform and benzene, less readily in absolute alcohol and ether, very slightly soluble in water, almost insoluble in light petroleum. One grm. of aconitine is dissolved by the following quantities of the respective liquids at 22–24°:—Ether (rel. dens. ·720), 63·9 grms.; alcohol (rel. dens. ·7945 at 21°), 37·04 grms.; light petroleum (rel. dens. ·670), 2806 grms.; benzene, 5·5 grms.; water, 726·4 grms. (Jurgens, Ar. Ph. [3] 24, 127, 172). 4431 grms. of water at 22° dissolve one grm. of pure aconitine (Dunstan a. Umney, C. J. 61, 385). The aqueous solution is alkaline to litmus. M.p. 183–184° (W. a. L.); 188·4° cor. (D. a. I.). Dextrorotatory; in alcoholic solution $[\alpha]_D = +11°$. Salts lævorotatory (D. a. I.).

Aconitine shows no distinctive colour reactions. Commercial specimens of aconitine vary much in composition, most of them being highly impure and non-crystalline. These contain, besides aconitine, the amorphous alkaloids isaconitine and aconine (Dunstan and Carr, C. J. 1893).

Aconitine is a most powerful poison. The poisonous dose is doubtful, as it is uncertain whether careful experiments have ever been made with a perfectly pure substance. Between $\frac{1}{20}$ and $\frac{1}{50}$ of a grain has been recorded as a fatal human dose. Minute quantities of the alkaloid, preferably in solution, when locally applied produce a characteristic tingling and numbness of the tongue and lips. This effect is so pronounced that it may be utilised in the detection of the alkaloid (Dunstan a. Harrison, C. J. 1893).

The ordinary salts of aconitine crystallise well. The *hydrobromide* $\bar{B}HBr,2\frac{1}{2}H_2O$ is lævorotatory $[\alpha]_D = -30{\cdot}47°$; m.p. 163° cor. (D. a. U.). The *hydriodide* is crystalline, and sparingly soluble in water. It is thrown down as a crystalline precipitate when potassium iodide and acetic acid are added to the not too dilute solution of an aconitine salt. The *aurichloride* $\bar{B}HAuCl_4$ is thrown down as a pale-yellow amorphous precipitate from solutions of the hydrochloride and auric chloride. It dissolves readily in alcohol and in chloroform, from which solutions it may be crystallised. M.p. 135·5° cor. (D. a. I.). The auric chloride compound ($\bar{B}.AuCl_3$) separates in crystals when alcoholic solutions of aconitine and auric chloride are mixed. M.p. 129° cor. (D. a. I.).

Reactions.—Aconitine is not altered at 100°, but when heated until it melts and kept for some time at this temperature it is gradually decomposed. Slowly hydrolysed by prolonged boiling with large quantities of water (D. a. I.). When heated in a closed tube for some hours at 140°, it is resolved by hydrolysis into aconine and benzoic acid

$$C_{33}H_{45}NO_{12} + H_2O = C_{26}H_{41}NO_{11} + C_7H_6O_2.$$

This reaction may be reversed, with formation of anhydro-aconitine, by heating aconine with ethyl benzoate (D. a. P.). More rapidly hydrolysed by alcoholic and aqueous alkalis even when cold, and also by mineral acids, both strong and dilute, especially when warm. When acids are used, dehydration simultaneously occurs, and some *apo-* or *anhydro-aconitine* is formed. Heated with acetic or benzoic anhydride, aconitine furnishes the acetyl or benzoyl derivative of anhydro- or apo- aconitine.

Detection and estimation.—When appreciable quantities of aconitine are obtainable, it may be identified by its melting-point and other properties, and those of its salts. The detection of very minute quantities, as in toxicology, is a matter of very considerable difficulty, and cannot at present be accomplished by chemical means. In these cases the characteristic physiological action is relied on (*v.* Stevenson, Guy's Hospital Reports [3] 26, 307). For the estimation of aconitine, Wright has proposed to hydrolyse the alkaloid with alcoholic potash, and then to isolate and weigh the resulting benzoic acid. This method is only applicable when it is certain that no other alkaloid yielding benzoic or other similar acid is present. For this reason it cannot be applied for the estimation of aconitine in the total alkaloids obtained from the plant, since benzoic acid is also yielded by isaconitine.

Anhydro- or apo- aconitine $C_{33}H_{43}NO_{11}$, the anhydride of aconitine, is the first product of the action of dilute mineral acids on aconitine. Its composition differs from that of aconitine by the absence of one molecular proportion of water. It is best prepared by heating aconitine with a saturated solution of tartaric acid in a closed tube at 100–110° for some hours (W. a. L.). When this acid is used, the aconitine does not suffer hydrolysis. The alkaloid is recovered from the liquid after the addition of ammonia in excess, by agitating with ether.

Properties.—Crystalline alkaloid forming crystalline salts, m.p. 185-186° (W. a. L.), 186·5° (cor.) (D. a. I.). The *aurichloride* ($\bar{B}.HAuCl_4$) is prepared by precipitation as a pale-yellow amorphous substance, which may be crystallised from its solution in absolute alcohol; m.p. 141°. When water as well as alcohol is present the crystalline *hydrated salt* ($\bar{B}.AuCl_3,H_2O$) is obtained; m.p. 129°. This salt is isomeric with aconitine aurochloride, into which it readily changes. The crystalline *auric chloride compound* ($\bar{B}.AuCl_3$) is obtained when alcoholic solutions of gold chloride and anhydro-aconitine are mixed; m.p. 147·5° (cor.) (D. a. I.). The physiological action of anhydro-aconitine appears to be quite as powerful as that of aconitine.

Aconine $C_{26}H_{41}NO_{11}$ or $C_{26}H_{39}NO_{11}$, the basic product of the hydrolysis of aconitine and isaconitine. An amorphous friable mass which forms salts which crystallise with difficulty (D. a. P.). Readily soluble in water, alcohol, and chloroform, but insoluble in ether (W. a. L.). The *aurichloride* ($\bar{B}.HAuCl_4$) is a pale-yellow precipitate which cannot be crystallised. Aconine is dextrorotatory, and its salts lævorotatory (D. a. P.). When heated with acids, aconine loses the elements of a molecule of water and yields *anhydro-aconine*, which is likewise an amorphous base. Benzoic anhydride converts aconine into a dibenzoyl derivative, probably identical with the benzoyl-anhydro-aconitine obtained by the action of the same reagent on aconitine (W. a. L.). Little is known as to the chemical structure of aconine. On oxidation it furnishes oxalic acid. When heated with ethyl benzoate in a closed tube it is converted into anhydro-aconitine (D. a. P.). It does not seem to be poisonous. Aconine occurs in small quantity in the roots of *A. Napellus* (D. a. U.).

Isaconitine and its salts are intensely bitter, but, unlike aconitine, produce no tingling sensation on the tongue, and are not poisonous in small doses (Dunstan a. Harrison, C. J. 63). Isaconitine $C_{33}H_{45}NO_{12}$ is isomeric with aconitine, and occurs to about the same extent as the alkaloid in the roots of *A. Napellus.*

Properties.—Amorphous friable resin forming crystalline salts. The base is dextrorotatory the salts lævorotatory. When hydrolysed it furnishes, like aconitine, *aconine* and *benzoic acid.* By reaction with auric chloride forms *aurochlorisaconitine* in colourless crystals, melting at 209°; is thus distinguished from aconitine, which yields an aurichloride.

Picraconitine $C_{31}H_{45}NO_{10}$(?). It is almost certain that this alkaloid does not exist in *A. Napellus.* It was obtained by T. B. Groves from a collection of roots stated to be those of *A. Napellus*, and was examined by Wright (C. J. 31, 143). It could not be obtained by Wright from other specimens, and was not found by Dunstan and Umney in the roots of specially grown plants. It is stated to be an uncrystallisable base, having a very bitter taste. It readily forms crystalline salts, and undergoes hydrolysis when it is heated with alkalis yielding benzoic acid and *picraconine* ($C_{24}H_{41}NO_9$), an amorphous base closely resembling aconine.

Pseudaconitine $C_{36}H_{49}NO_{12}$, the principal alkaloid of *A. ferox*, the so-called 'bish' or Indian aconite. The roots of this plant contain about ·2 p.c. of this alkaloid, together with amorphous bases, about which little or nothing is known. It closely resembles aconitine in its principal physical and chemical properties, and also in its physiological action, being at least as toxic. It may be extracted from the plant by processes similar to those described for aconitine.

Properties.—Crystals containing one mol. prop. of water, m.p. 104–105°. Nearly insoluble in water, soluble in alcohol, ether, and chloroform. The ordinary salts crystallise with difficulty, the nitrate ($\breve{B}.HNO_3,3H_2O$) most readily. The aurichloride ($\breve{B}.HAuCl_4$) may be crystallised from alcohol (Wright a. Luff, C. J. 33, 151, 318).

Reactions.—Hydrolysed by alcoholic potash, or less readily by mineral acids, with production of a base *pseudaconine* and *di-methyl-protocatechuic acid* (veratric acid) $C_{36}H_{49}NO_{12} + H_2O = C_{27}N_{41}NO_9 + C_9H_{10}O_4$. Acetic or benzoic anhydrides convert pseudaconitine into acetyl or benzoyl derivatives of anhydro-pseudaconitine.

Anhydro-pseudaconitine $C_{36}H_{47}NO_{11}$ is produced like the anhydride of aconitine when the alkaloid is heated with acids. It crystallises with $1H_2O$, and melts at 102–103° (W. a. L.).

Pseudaconine $C_{27}H_{41}NO_9$ the basic product of the hydrolysis of pseudaconitine. It resembles aconine in many respects, but differs from it in crystallising, although with difficulty. Its salts are amorphous. The free base is alkaline, and acts as a reducing agent on salts of silver, platinum, gold, &c. When strongly heated with alcoholic soda it loses a molecule of water, and becomes anhydro-pseudaconine $C_{27}H_{39}NO_8$ (W. a. L.).

Japaconitine $C_{66}H_{88}N_2O_{21}$, the principal alkaloid of Japanese aconite root, sometimes called *Aconitum japonicum*, although the botanical origin of the Japanese roots is unknown. It may be separated from the root, which also contains amorphous alkaloids, by the process of extraction described for aconitine. About ·1 per cent. appears to be present (Wright a. Luff, C. J. 35, 387). Lubbe (C. C. 1890, ii. 148) has obtained from the Japanese plant 'kusa-uzu' an alkaloid which he considers to be identical with aconitine, and represents by the formula $C_{33}H_{44}NO_{12}$(?).

Properties.—Crystals, m.p. 184–186°. Nearly insoluble in water, soluble in alcohol, ether, and chloroform. Like aconitine, and unlike pseudaconitine, its ordinary salts readily crystallise.

Reactions.—Japaconitine differs from both aconitine and pseudaconitine in not furnishing an anhydride when it is heated with acids. The action of alcoholic potash on japaconitine in a closed tube at 100° leads to its hydrolysis, with formation of *benzoic acid* and *japaconine*, a base which has much in common with aconine. Japaconine and its salts are amorphous. By the action of benzoic anhydride it yields a tetrabenzoyl derivative, and in this respect differs from aconine and pseudaconine, which furnish only dibenzoyl derivatives. Wright a. Luff suggest that as japaconitine does not form an anhydride, it may itself be an anhydro- compound resulting from the condensation of two molecules of a hypothetical alkaloid having the formula $C_{33}H_{47}NO_{12}$, thus

$$2C_{33}H_{47}NO_{12} = 3H_2O + C_{66}H_{88}N_2O_{21}.$$

Such a base could not, however, be found in the roots. Japaconitine exerts a physiological action very similar to that of aconitine, and seems to be equally poisonous. Indeed, the differences in physiological action which might be expected to result from the different composition of aconitine pseudaconitine, and japaconitine have not yet been demonstrated. At present we only know that the main effect is the same in the three cases, and that the removal of the benzoyl or veratryl groups from these alkaloids furnishes a base (aconine, pseudaconine, or japaconine) which fails to exert the characteristic physiological action, and, in fact, is not poisonous.

Lycaconitine $C_{27}H_{34}N_2O_6,2H_2O$ and **Myoctonine** $C_{27}H_{30}N_2O_8,5H_2O$ are two little-known amorphous alkaloids contained in *A. lycoctonum* (Dragendorff a. Spohn, P. Z. 23).

Adenine *v. Caffeïne.*

Arecaïne $C_7H_{11}NO_2$ occurs in areca nuts (*Areca Catechu*); crystals; m.p. 213°. Easily soluble in water, insoluble in absolute alcohol, ether, chloroform, and benzene. A feeble monacidic base, whose salts are crystalline. It is not poisonous.

Arecoline $C_8H_{13}NO_2$ is the poisonous alkaloid of areca nuts. It is a strong base, which forms crystalline salts very soluble in water. Arecoline is a powerful poison. When it is heated with hydriodic acid, methyl iodide is formed, together with *arecaïdine* ($C_7H_{11}NO_2$), an isomeride of arecaïne, which is also found in areca nuts. *Guvacine* $C_6H_9NO_2$ is a fourth alkaloid contained in the areca nuts (Jahns, B. 21, 3404; 23, 2972; 24, 2615).

Aricine $C_{23}H_{26}N_2O_4$ is an alkaloid found in cusco bark and cuprea bark, which originate with plants closely allied to the cinchonas. Crystals, m.p. 188°; lævorotatory in alcoholic solution, $[\alpha]_D = -58{\cdot}18°$. The salts are crystalline, and dextrorotatory (Hesse, A. 185, 320; Moissan a. Landrin, C. R. 110, 469).

Aspidospermine $C_{22}H_{30}N_2O$ and **Aspidospermatine** $C_{22}H_{28}N_2O_2$ are two of a number of alkaloids found in quebracho bark (*Aspidosperma quebracho*) (Fraude, B. 11, 2190; 12, 1560; Hesse, A. 211, 249).

Atropine and the **Solanaceous alkaloids** *v.* also *Datura Stramonium.*

Atropine $C_{17}H_{23}NO_3$, the chief alkaloid contained in *Atropa Belladonna* and in *Datura Stramonium*. First obtained by Mein in 1886 (A. 6, 67). *Daturine*, the supposed alkaloid of *Datura Stramonium*, has been shown by Ladenburg (B. 13, 909) to be a mixture of hyoscyamine and atropine. The isomeric alkaloid, hyoscyamine, is often found with atropine in plants.

Preparation.—Many processes have been suggested for isolating atropine from the leaves and root of *Atropa Belladonna*, and from the seeds of *Datura Stramonium*. The simplest is that suggested by Pesci (Gazzetta, 10, 426), which was originally proposed for the leaves, but with certain modifications it can also be applied for the extraction of the alkaloid from the root and seeds.

The finely powdered substance is exhausted by percolation with water, which dissolves the alkaloidal salts. The aqueous solution is evaporated to a small volume, and made alkaline with ammonia. It is then extracted with benzene, which dissolves the alkaloids. The benzene is shaken with very dilute sulphuric acid, when the alkaloids pass as sulphates out of the benzene into the aqueous layer, any resin, fat, &c., remaining dissolved in the benzene. The acid liquid is now made alkaline with sodium carbonate, and the alkaloid removed by shaking with chloroform. The chloroform when evaporated leaves a residue of the total alkaloids (atropine, hyoscyamine, &c.), or if light petroleum is added to the solution in chloroform, the greater part of the atropine crystallises out, leaving the other alkaloids dissolved. It is safer to use ammonia than sodium carbonate to liberate the alkaloid from the acid solution, and when the root or seeds are being worked upon, it is better to exhaust with alcohol instead of water; the alcohol is distilled, the residue extracted with water, and the aqueous liquid dealt with as above described.

Ladenburg (A. 206, 274) finally purifies atropine by repeatedly crystallising it from dilute alcohol (50 p.c.) in which the other alkaloids, especially hyoscyamine, are more soluble.

The amount of atropine contained in the different parts of the belladonna plant varies with its growth. The maximum quantity is found in the root collected in autumn (·2–·4 p.c.). The ripe fruit may contain as much as 1 p.c. (Schütte, Ar. Ph. 229, 492). Stramonium seeds contain rather less than ·5 p.c. of alkaloid (Schmidt, A. 208, 196). Günther (Vierteljährschrift f. Pharmacie, 19, 598) has estimated the quantity of atropine in the different parts of *Atropa Belladonna* with the following results: Leaves, ·2 p.c.; stem, ·04 p.c.; unripe fruit, ·19 p.c.; ripe fruit, ·21 p.c.; seeds, ·33 p.c.; root, ·06 p.c. In *Datura Stramonium* the same observer found in the leaves ·07 p.c.; stem, ·02 p.c.; seeds, ·25 p.c.; root, ·02 p.c.

Dunstan and Ransom (Ph. [3] 14, 623) found ·22 p.c. of total alkaloids in the dry leaves of *Atropa Belladonna*, and ·38, ·35, and ·39 p.c. in different specimens of the dry root.

Properties.—Prismatic crystals; m.p. 114° (Ladenburg, A. 206, 274), 115·5° (Hesse, A. 271, 100). Readily soluble in alcohol and chloroform, less soluble in ether and hot water, sparingly soluble in cold water. The aqueous solution is alkaline to litmus, and has a very bitter taste. Atropine is optically inactive (Ladenburg, B. 21, 3065). Lævorotatory $[\alpha]_D = -1·89$ (Will, B. 21, 1717, 2777); $[\alpha]_D = -0·4°$ in alcohol (Hesse, A. 271, 100). The alkaloid is best crystallised from its solution in weak alcohol. It is slightly volatile with steam (Dragendorff). One of the most remarkable properties of atropine is that of causing dilatation of the pupil of the eye, a property which is often made use of in detecting it and other alkaloids of this group, several of which exert this mydriatic action. A drop or two of an aqueous solution, containing 1 part of atropine in 130,000 parts of water, when introduced into the eye of a cat is sufficient to produce this effect. When taken internally atropine is highly poisonous; some of the alkaloid is apparently excreted unchanged in the urine.

The ordinary salts of atropine are crystalline and soluble in water. The *aurichloride* ($B.HAuCl_4$) appears as an oily precipitate when produced in the ordinary manner. This soon solidifies to a crystalline mass, which may be recrystallised from water acidulated with hydrochloric acid. The crystals melt at 135°, or below 100° when heated under water (Ladenburg, A. 206, 274); near 138° (Hesse, A. 271, 100). This salt is well adapted for the identification of the alkaloid, since the aurichlorides of the other alkaloids of this group melt at different temperatures.

Reactions and constitution.—Among the characteristic qualitative reactions of atropine may be mentioned the production of an odour of heliotrope or of bitter almond oil, when a solution of the alkaloid is warmed with sulphuric acid and a fragment of potassium bichromate or permanganate. When the alkaloid is evaporated to dryness with a few drops of fuming nitric acid a residue is obtained which turns violet (changing to red) when it is moistened with alcoholic potash (Vitali, Fr. 1881, 563). Many alkaloids form white insoluble compounds with mercuric chloride, but when a dilute alcoholic solution of mercuric chloride is added to a solution of atropine (not a salt) and the mixture is warmed, a yellowish-red precipitate of mercuric oxide is thrown down, and after a time a colourless crystalline double salt separates from the solution (Gerrard, Ph. [3] 14, 718).

Atropine is capable of yielding an anhydride (apo-atropine) when heated with dilute nitric acid. It readily undergoes hydrolysis when warmed with alkalis or strong acids. By heating it with concentrated hydrochloric acid in a closed tube at 130°, or with baryta-water at 60°, it is completely resolved into the base *tropine* ($C_8H_{15}NO$) and *tropic acid* (phenyl-hydroxy-propionic acid)

$$C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_9H_{10}O_3.$$

At higher temperatures than these, or after prolonged heating, the tropic acid suffers dehydration, forming, when alkalis are used, *atropic acid* ($C_9H_8O_2$), or in presence of acids, the isomeric *isatropic acid.*

Tropine $C_8H_{15}NO$ forms crystals which melt at 61·2°, producing a liquid which boils at 229°. The crystals are soluble in water, alcohol, and ether. Tropine is a strong base, which forms crystalline salts. It is poisonous, but does not dilate the pupil of the eye. When tropine and tropic acid are mixed they unite to form the tropate of tropine ($C_8H_{15}NO.C_9H_{10}O_3$), and this salt, when heated with dilute hydrochloric acid, loses water and furnishes atropine, identical with the natural alkaloid (Ladenburg, A. 217, 74). Similarly, by heating other organic salts of tropine with dilute hydrochloric acid, dehydration occurs, with production of the acid derivative of tropine. The bases thus formed by introducing acid radicles into the molecule of tropine have been called by Ladenburg *tropeïnes.* Several of the tropeïnes exert a mydriatic action. The *phenyl-glycollic tropeïne* ($C_{16}H_{21}NO_3$) has been used in surgery under the name of *homatropine.* Its mydriatic effect is less persistent than that of atropine (Ladenburg, A. 217, 74). It appears that only those tropeïnes produce a mydriatic effect which contain an alcoholic (not phenolic) hydroxyl in the acid group.

When tropine is heated with sulphuric acid it loses water, and gives rise to a new base *tropidine* ($C_8H_{13}N$), which is an oily liquid smelling like conine, b.p. 162–163°. This base has been shown by Ladenburg to be the ethylene (or ethylidene) methyl derivative of tetrahydropyridine $C_5H_6(C_2H_4)N.CH_3$ (B. 15, 1140; 23, 1780). Tropine is the hydroxy- derivative of this substance, the hydroxyl being in union with the ethylene or ethylidene group. Hence the probable formula for tropine is $C_5H_7(C_2H_4OH)N.CH_3$, which represents it as the hydroxy-ethyl methyl derivative of tetrahydropyridine. Atropine is the tropyl-tropeïne of this base,

$$C_5H_7C_2H_4O(C_9H_9O_2)N.CH_3.$$

Ladenburg (B. 22, 2590) has recently prepared two optically active tropic acids (the ordinary variety is inactive). From the reaction of dextro- tropic acid and tropine he has formed a dextrorotatory atropine, whilst the lævorotatory tropic acid has furnished a lævo- atropine. These bases resemble natural atropine in many respects, but differ, not only in being optically active, but also in their melting-points and those of their aurichlorides. Although the constitution of atropine has been ascertained, its complete synthesis has not yet been achieved.

Detection and estimation of atropine.—Atropine may be detected by means of the reactions referred to above, after it has been isolated in a fairly pure state. Proof of its identity is most readily obtained by means of determination of the melting-point of its recrystallised aurichloride.

For the accurate estimation of atropine and hyoscyamine in plants, and in medicinal preparations made from them, Dunstan and Ransom have devised the following methods (Ph. [3] 14, 623; 16, 237, 238, 777).

For the root. Exhaust by hot percolation 20 grms. of the finely-powdered root with a mixture of equal parts of chloroform and absolute alcohol, which readily dissolves the alkaloidal salts. Agitate the solution with 25 c.c. of water, when the salts pass into the aqueous layer, and the resin, fat, colouring matter, &c., remain dissolved in the chloroform. Repeat this extraction with water. Wash the 50 c.c. of water with a little pure chloroform to remove adhering impurity, then add ammonia in slight excess, and dissolve out the liberated alkaloids by agitation with chloroform in the usual way. The residue of alkaloid left on the evaporation of the chloroform is dried at 100° and weighed (Ph. [3] 14, 623).

For the leaves. Twenty grms. of the finely-powdered dry leaves are exhausted with absolute alcohol. The liquid is largely diluted with water, acidulated with hydrochloric acid, and repeatedly extracted by agitation with chloroform until the whole of the chlorophyll, fat, &c., has been removed. The liquid is then made alkaline with ammonia and extracted with chloroform, which, on evaporation, leaves a residue of alkaloid. This must be dried at 100° before being weighed (Ph. [3] 16, 237).

For the alcoholic extract of the leaves. From 1 to 2 grms. of the extract are dissolved, as far as possible, in warm dilute hydrochloric acid, any residue being extracted with the dilute acid until all the alkaloid has been dissolved. The acid liquid is then extracted with chloroform until nothing further is removed, and, after this treatment, is made alkaline with ammonia and the free alkaloid removed by agitating again with chloroform, which on evaporation leaves a residue of alkaloid that is dried at 100° and weighed (Ph. [3] 16, 238).

For the alcoholic extract of the root. Two grms. of this extract are dissolved as far as possible in dilute hydrochloric acid. The acid liquid is then dealt with in the manner described in connection with the estimation of the alkaloids in the extract of the leaves (Ph. [3] 16, 777).

Hyoscyamine $C_{17}H_{23}NO_3$. An isomeride of atropine, with which it occurs in *Atropa Belladonna* and in *Datura Stramonium* (Ladenburg, B. 13, 909; Schmidt, A. 208, 196). It is also present in henbane, *Hyoscyamus niger*, in *Duboisia myoporoides* (Ladenburg a. Peterson, B. 20, 1661), the so-called 'duboisine' being a mixture of this alkaloid with hyoscine; in *Scopola carniolica* (Dunstan a. Chaston, Ph. [3] 20, 461), in *Scopola Hladnikiana* and *S. japonica* (Schmidt, Ar. Ph. [3] 26, 185, 214), and in other similar plants; also in lettuce, *Lactuca virosa* and *L. sativa* (Dymond, C. J. 61, 90). Evidence has been recorded which seems to show that sometimes both atropine and hyoscyamine, and at other times only one of these alkaloids, may be present in the same plant at different stages of its growth, hyoscyamine being found in the young plant and atropine chiefly in old roots (Siebert, Ar. Ph. [3] 28, 145; Schütte, Ar. Ph. 229, 492). The leaves and root of *Hyoscyamus niger* contain, as a rule, about ·2 p.c. of this alkaloid. Hyoscyamine is sometimes commercially called 'light atropine.' The pure alkaloid is very rarely, if ever, met with in commerce, being nearly always contaminated with atropine or hyoscine.

Preparation.—Hyoscyamine may be extracted from the various plants containing it by means of the process described for atropine. Ammonia should be used to liberate the alkaloid, and not fixed alkalis or their carbonates. When atropine and hyoscine are also present in the plant these alkaloids are obtained with the hyoscyamine. The isolation of pure hyoscyamine from the mixture of the alkaloids is a difficult operation. The greater part of the atropine may be removed by repeated crystallisation from dilute alcohol, the hyoscyamine for the most part remaining dissolved. The isolation of perfectly pure hyoscyamine can only be certainly accomplished by converting the alkaloid into the aurichloride and repeatedly crystallising this salt from dilute hydrochloric acid until it melts at the proper temperature. The alkaloid may be regenerated from the aurichloride by decomposing it with hydrogen sulphide in the usual manner.

Properties.—Long, silky crystals; m.p. 108·5° (Ladenburg, A. 206, 274); lævorotatory $[\alpha]_D = -14·5°$ (Ladenburg), $[\alpha]_D = -20·97°$ (Will, B. 21, 1717); $[\alpha]_D = -20·3°$ (Hesse, A. 271, 100). Readily soluble in benzene, chloroform, and alcohol, less readily in ether and cold water. When heated the alkaloid sublimes, with partial decomposition, and it is said to be slightly volatile with steam. When hyoscyamine is heated to a temperature slightly higher than its melting-point, it is converted into atropine (Schmidt, B. 21, 1829). This conversion also takes place with great facility when hyoscyamine is warmed, or even allowed to stand in the cold, with fixed alkalis and alkali carbonates, but it only takes place extremely slowly in presence of ammonia (Will, B. 21, 1717, 2777). The atropine thus produced is stated by Will to be slightly lævorotatory, $[\alpha]_D = -1\cdot98$. Ladenburg has, however, questioned the accuracy of the statement, asserting that atropine, when pure, is inactive. Hyoscyamine exerts a strong mydriatic action, and is a powerful poison.

Many of the ordinary salts of hyoscyamine are crystalline and soluble in water. The *sulphate* ($\bar{B}_2.H_2SO_4$) crystallises well from alcohol and melts at 206° (Will, B. 21, 1717). The *aurichloride* ($\bar{B}.HAuCl_4$) is best crystallised from dilute hydrochloric acid. It melts at 159-160° (Ladenburg, *l.c.*); 162° (Will, *l.c.*), 159° (Hesse, *l.c.*), but, unlike atropine aurichloride, it does not melt when heated under water. This salt is less soluble in acidulated water than atropine aurochloride, from which it may be separated by repeated crystallisation.

Reactions.—The qualitative reactions of hyoscyamine are, for the most part, identical with those of atropine. When heated with acids or alkalis, like atropine it undergoes hydrolysis into *tropine* and *tropic acid*. On reversing this reaction by heating together the tropine and tropic acid, atropine and not hyoscyamine is formed. It is, indeed, probable that the hyoscyamine is in the first place converted by these reagents into atropine, and that it is really this alkaloid which is hydrolysed.

Detection and estimation.—Hyoscyamine may be detected by its mydriatic action and by most of the reactions described under atropine. Its partial separation from atropine may be effected by recrystallisation from dilute alcohol, but it can only be completely separated and identified by preparing its aurichloride, which is characterised by its melting-point (for details of this method of separation *v.* Dunstan a. Chaston, Ph. [3] 20, 461).

For the estimation of hyoscyamine in plants and in medicinal preparations the methods described for atropine are applicable. (For an optical method *v.* Hesse, *l.c.*)

Hyoscine $C_{17}H_{23}NO_3$, the second isomeride of atropine, with which it occurs in henbane and in other plants. It constitutes the greater part of the 'amorphous hyoscyamine' of commerce.

Preparation.—The total alkaloid is separated from the plant by the method described for atropine. The hyoscine remains in the alcoholic solution when the atropine and hyoscyamine have crystallised out. The hyoscine is completely purified by conversion into the aurichloride, which is crystallised until it has the proper melting-point, the alkaloid being regenerated in the usual way.

Properties.—Colourless syrup, not crystallisable. Soluble in alcohol and ether, slightly soluble in water (Ladenburg, B. 13, 909, 1549; 14, 1870). Hard transparent resin melts near 55°, forming a mobile liquid. In alcoholic solution detrorotatory $[\alpha]_D = -13\cdot7°$; the rotation is much diminished by addition of soda (Hesse). Its mydriatic power is stated to be greater than that of atropine. The ordinary salts of hyoscine are crystalline. The *hydriodide* $\bar{B}.HI,H_2O$ is lævorotatory. The *hydrobromide* $\bar{B}.HBr3H_2O$ is dextrorotatory. In water $[\alpha]_D = -22\cdot5°$ (Hesse). The *aurichloride* ($\bar{B}.HAuCl_4$) is less soluble than the corresponding hyoscyamine compound. It crystallises well from dilute hydrochloric acid; m.p. 198° (Ladenburg, *l.c.*).

Reactions.—Hyoscine for the most part reacts like atropine and hyoscyamine, but it does not precipitate mercuric oxide from mercuric chloride. When hydrolysed by acids or alkalis it yields *tropic acid* and *pseudo-tropine*, an isomeride of tropine, which melts at 106°. When this reaction is reversed, an isomeride of hyoscine is obtained (Liebermann and Limpach, B. 25, 927).

Detection and estimation.—Hyoscine is readily distinguished from its isomerides by the higher melting-point (198°) of its aurichloride. At present the repeated recrystallisation of this salt, until it has the proper melting-point, is the only known method of purifying the alkaloid. No accurate process of estimation has yet been devised.

According to Schmidt (Ar. Ph. 230, 207) hyoscine is at present unknown. Commercial hyoscine chiefly consists of an alkaloid *scopolamine* $C_{17}H_{21}NO_4$, which crystallises when pure and furnishes crystalline salts. On hydrolysis it furnishes a new base *scopoline* and *atropic acid*. The same alkaloid has been obtained from belladonna, hyoscyamine, and other solanaceous plants (*v.* also Hesse, 271, 100).

Belladonnine $C_{17}H_{23}NO_4$? This alkaloid is stated to occur in the leaves and root of *Atropa Belladonna* (Kraut, B. 13, 165; Dürkopf, B. 22, 3183; Hesse, A. 262, 100). According to Merling (B. 17, 381), it has the formula $C_{17}H_{21}NO_2$, and is isomeric with anhydro-atropine, but Ladenburg and Roth (B. 17, 152) assert that it is an oxy-atropine ($C_{17}H_{23}NO_4$). Belladonnine is a resinous uncrystallisable base, which is hydrolysed with much greater difficulty than the other atropaceous alkaloids, yielding oxytropine ($C_8H_{15}NO_2$) and tropic acid. It appears to be devoid of mydriatic power.

Closely resembling belladonnine is the new alkaloid recently obtained from the root of *A. Belladonna*, and described by Hesse (A. 261, 87; 262, 100) under the name of *atropamine*

($C_{17}H_{21}NO_2$).

It is an amorphous solid, melting at 60°, and furnishing crystalline salts. The alkaloid is optically inactive, and does not dilate the pupil. When hydrolysed with strong hydrochloric acid it yields β-tropine and atropic acid. Atropamine may possibly be anhydro-hyoscine. Acids are said to convert it into the belladonnine of Merling.

Both belladonnine and atropamine require further examination.

Bebeerine *v.* *Buxine.*

Berberine and the Berberis Alkaloids.

Berberine $C_{20}H_{17}NO_4$ is contained in various species of *Berberis*, especially in *Berberis vulgaris* (barberry) together with *oxyacanthine* in *Calumba* root, in *Hydrastis canadensis*, together with hydrastine in *Coptis tecta*, which contains as much as 8 p.c., and in a large number of other plants.

Preparation.—The best available materials from which to extract berberine are the root of *Hydrastis canadensis*, which contains about 4 p.c. of the alkaloid, and the root of *Berberis vulgaris*. The finely powdered hydrastis root is exhausted with alcohol, the greater part of the alcohol removed by distillation, and the alkaloid converted into sulphate or nitrate by the addition of sufficient dilute sulphuric acid or nitric acid. The berberine salt which separates is collected, washed, and the alkaloid liberated by the addition of ammonia. The precipitated alkaloid is again converted into the nitrate or sulphate, and the alkaloid regenerated by ammonia. The berberine is finally crystallised from water or alcohol. In this process the hydrastine salt being more soluble, is not precipitated (Lloyd, Ph. 3, 10, 125; Perrins, C. J. 15, 339).

Barberry root is exhausted with boiling water, the liquid evaporated to a small volume, and the berberine precipitated from it by adding strong alcohol. The yellow precipitate of alkaloid is purified by crystallisation from water or alcohol, or, better, by converting it into the sulphate, which is repeatedly crystallised (Buchner, A. 24, 228).

Properties.—Long, silky, yellow, needle-shaped crystals. Crystallised from water the substance contains $5\frac{1}{2}H_2O$; dried at 100° the crystals retain $2\frac{1}{2}H_2O$ (Perkin, C. J. 55, 63); m.p. 120° (Fleitmann, A. 59, 160). Decomposes before melting (Perkin, *l.c.*). Slightly soluble in cold water and alcohol, but freely soluble in the hot liquids; slightly soluble in benzene and chloroform; insoluble in ether and light petroleum. Its aqueous solution is neutral to litmus, optically inactive, and has a bitter taste. The alkaloid is not poisonous to man, and is medicinally used, like preparations of the plants containing it, as a tonic. The ordinary salts of berberine crystallise well, and are of a yellow or red colour. They are sparingly soluble in water, especially in presence of mineral acids and salts. For the properties of the salts see the papers above referred to, and also Hlasiwetz, A. Suppl. 2, 191; Schmidt a. Kerstein, Ar. Ph. [3] 28, 49.

Reactions.—Alkalis colour berberine brown. On adding excess of hydrochloric, or sulphuric, or nitric acids to a solution of berberine the salts separate as yellow crystalline precipitates. Chlorine water added to a solution of the hydrochloride produces a bright-red colouration, which is seen in very dilute solutions.

Berberine is not decomposed by aqueous acids or alkalis. When distilled with alkali it furnishes quinoline (? iso-quinoline). On reduction with metal and acid a crystalline tetra-hydride

$(C_{20}H_{21}NO_4)$

is formed (Hlasiwetz a. Gilm, A. 115, 45; 122, 256 *et l.c. supra*). On oxidation with alkaline permanganate berberine yields principally *hemipinic acid* $(C_{10}H_{10}O_6)$, which is also obtained by oxidising narcotine. This dibasic acid furnishes protocatechuic acid when fused with alkali, and contains two methoxyl groups (Perkin, *l.c.*). *Berberal* $(C_{20}H_{17}NO_7)$ and *berberilic acid*

$(C_{20}H_{19}NO_9)$,

two iso-quinoline derivatives, are also products of the oxidation of berberine. A thorough examination of its oxidation products has led to the conclusion that berberine contains a nucleus of iso-quinoline, to which is attached a benzene ring bearing two methoxyl groups. Berberine is therefore closely allied to hydrastine, which occurs with it in *Hydrastis canadensis*, and also to the two opium alkaloids, papaverine and narcotine, all of which appear to be benzene derivatives of iso-quinoline (Perkin, C. J. 57, 992).

Hydrastine $C_{21}H_{21}NO_6$, an alkaloid occurring, together with berberine, in the root of *Hydrastis canadensis* to the extent of about 1 p.c.

Preparation.—Hydrastine may be isolated from the mother-liquid from which the berberine salt has crystallised (*v. supra*). This is largely diluted with water, and almost neutralised with ammonia. On evaporation, ammonium sulphate, resin, &c., separate out; these are removed, and the hydrastine precipitated from the cold liquid by ammonia. The coloured precipitate is dissolved in alcohol, and the colouring matter removed by digestion with animal charcoal; the alkaloid crystallises from the concentrated solution. In order to purify it, the hydrastine is repeatedly crystallised from alcohol.

According to Freund and Will (B. 19, 2797), hydrastine is most readily obtained by percolating finely-powdered hydrastis root with ether, and crystallising the ethereal residue from alcohol.

Properties.—Colourless, prismatic crystals; m.p. 132°. Insoluble in water; readily soluble in chloroform and benzene; less soluble in ether and alcohol. The alcoholic solution is alkaline to litmus and lævorotatory; in chloroform $[\alpha]_D = -67{\cdot}8°$.

The ordinary salts of hydrastine are soluble in water, but do not crystallise. They are poisonous to animals (Perrins, Ph. [2] 3, 546; Mahla, Am. S. 36, 57; Lloyd, Proc. Am. Pharm. Assoc. 26, 805; Power, Ph. [3] 15, 297; 16, 1092; Schmidt a. Kerstein, Ar. Ph. [3] 28, 49).

Reactions.—When chlorine water is added to an aqueous solution of hydrastine hydrochloride, a blue fluorescence is observed. Potassium chromate forms a yellow precipitate in solutions of hydrastine salts. For other colour reactions of hydrastine, *v.* Lyons, Ph. [3] 16, 880.

The principal product of the oxidation of hydrastine is *opianic acid*

$(C_{10}H_{10}O_5$ or $C_6H_2(CHO)(OCH_3)_2CO_2H)$,

which also results from the oxidation of narcotine, to which hydrastine bears a great resemblance; by further oxidation, opianic acid yields *hemipinic acid* $(C_6H_2(OCH_3)_2(CO_2H)_2)$. When nitric acid is used to oxidise hydrastine, a new base, *hydrastinine* $C_{11}H_{13}NO_3$, is also formed:

$$C_{21}H_{21}NO_6 + H_2O + O = C_{10}H_{10}O_5 + C_{11}H_{13}NO_3.$$

This substance is a derivative of pyrocatechol, and closely resembles cotarnine obtained under similar conditions from the opium alkaloid narcotine, which is probably its methoxyl derivative (Freund a. Will, B. 19, 27, 97; 20, 88, 2400. See also *Narcotine*, under *Morphine and the opium alkaloids*). When hydrastine is fused with potash, *proto-catechuic acid* and *formic acid* are produced.

The later researches of Freund point to the conclusion that, although hydrastinine is a derivative of pyrocatechol, in reacting with opianic acid it becomes an iso-quinoline derivative. The so-called ordinary salts of hydrastinine, formed with the elimination of the elements of one molecule of water, have proved to be in reality isoquinoline derivatives. This nucleus must therefore be present in hydrastine joined to a residue of opianic acid (Freund, B. 22, 2329; 23, 404; 24, 2730).

Oxyacanthine $C_{18}H_{19}NO_3$ accompanies berberine in *Berberis vulgaris* (Polex, Ar. Ph. 45, 271; Hesse, B. 19, 3190). It may be obtained by precipitating with soda the mother-liquor from which all the berberine salt has crystallised (Hesse). It is a white powder, m.p. 139°, which crystallises with difficulty from alcohol or ether. The crystals melt at 208–214° (Hesse). Oxyacanthine is insoluble in water, easily soluble in chloroform, less soluble in alcohol. The alcoholic solution is dextrorotatory, alkaline to litmus, and has a very bitter taste. The ordinary salts crystallise well.

Berbamine $C_{18}H_{19}NO_3$ (Hesse, B. 19, 3193) is a third alkaloid contained in *Berberis vulgaris*.

Caffeïne, see *Theobromine and the alkaloids of tea and coffee, infra.*

CONINE AND THE ALKALOIDS OF HEMLOCK.

Conine or **Coniine** $C_8H_{17}N$ is the principal poisonous volatile alkaloid of hemlock, *Conium maculatum*. So far this alkaloid has not been found in any other plant. For many years its formula was thought to be $C_8H_{15}N$. Its true composition was first demonstrated by Hofmann in 1881 (B. 14, 705). Besides conine, hemlock contains three other alkaloids, viz. *methyl-conine*, *conydrine*, and *pseudo-conydrine*. Hemlock seeds contain about 1 p.c. of conine.

Preparation.—Conine is most readily separated from the crushed hemlock seeds by digesting them with water made alkaline with sodium carbonate, to decompose the malate of conine, and distilling the mixture in a current of steam. The distillate contains the conine, together with much ammonia derived from the ammonium salts present in the seeds. The liquid is neutralised with hydrochloric acid, and evaporated to dryness. The dry residue is extracted with absolute alcohol, when most of the ammonium chloride remains undissolved, whilst the alkaloidal hydrochlorides go into solution. If ether is added to the alcoholic solution, a further quantity of ammonium chloride is separated. The residue left by the evaporation of the alcoholic solution is dissolved in cold water, ether added, and the conine liberated by the addition of potash. The ethereal layer is decanted, washed, dried with potassium carbonate and distilled at a low temperature, when the conine remains as an oily liquid. It may be purified from the accompanying conydrine by fractional distillation; the conine passes over first. Another method consists in extracting the powdered seeds with dilute acetic acid. The liquid is distilled under reduced pressure at as low a temperature as possible, the resulting syrup mixed with magnesia, and extracted with ether. The ethereal solution is then treated as described above (Schorm, B. 14, 1765; see also HEMLOCK).

Properties.—Colourless, alkaline liquid, having a remarkable penetrating odour and a burning taste; b.p. 166–167°; rel. dens. ·8626 at 0° (Ladenburg, B. 19, 2578); dextrorotatory $[\alpha]_D = +13·79°$.

Conine is slightly soluble in cold water, but is less soluble in hot water, so that a clear cold solution becomes turbid when warmed. Conine is capable of dissolving about one-quarter of its own volume of water at the ordinary temperature. When boiled with water, the alkaloid distils with the steam. Conine mixes with alcohol in all proportions, and is also readily soluble in ether, but only sparingly in chloroform and carbon disulphide. Exposed to the air, conine darkens and slowly resinifies. When administered internally, conine acts as a powerful poison. It is a monacidic base. The ordinary salts are crystalline, and soluble in water and alcohol. The *hydrochloride* B.HCl melts at 208–209° (Ladenburg).

Reactions.—Conine is a strong base, which precipitates many metallic hydroxides from solutions of their salts. Sulphuric acid colours conine dark red. Dry hydrogen chloride produces a red colour, changing to a dark blue.

Conine is a secondary base, and combines with two molecules of methyl iodide to form the 'ammonium' compound. When oxidised with nitric acid, conine affords *normal butyric acid* among other products. When permanganate is used, *α-pyridine-carboxylic acid* (*picolinic acid*) is obtained.

When conine is distilled with zinc-dust an unusual result is observed. The conine is decomposed into hydrogen, and α-normal propyl pyridine (conyrine).

Ladenburg has inferred from the above-mentioned and other reactions that conine is the α-normal propyl derivative of hexahydropyridine (piperidine), and he has confirmed the accuracy of this inference by effecting the synthesis of the alkaloid by hydrogenating (with sodium in alcoholic solution) α-allyl pyridine $C_5H_4N(C_3H_5) + 4H_2 = C_5H_{10}N(C_3H_7)$. The liquid thus produced possesses all the chemical and physical properties of the natural alkaloid except one: it is optically inactive (Ladenburg, B. 19, 2579). Ladenburg has since succeeded in resolving the inactive conine into dextrorotatory conine and lævorotatory conine, and has shown the dextro-compound to be identical with the natural alkaloid. This separation was effected by Pasteur's method of fractionally crystallising the two enantiomorphic tartrates (Ladenburg, B. 19, 2579).

Methyl conine $C_8H_{16}(CH_3)N$ is stated to occur in hemlock (*v.* Planta a. Kekulé, A. 89, 129). It is a colourless, oily liquid, closely resembling conine.

Conydrine or **Conhydrine** $C_8H_{17}NO$, which is also found in hemlock is the hydroxyl derivative of conine ($C_8H_{16}(OH)N$). In the extraction of conine from hemlock it is also removed. It may be separated either by cooling the concentrated ethereal solution of the two alkoloids, when the conydrine crystallises out, or it may be obtained by distilling the crude conine, when it remains behind in the retort, if the temperature has not exceeded 180°.

Conydrine is a solid crystalline, strongly basic substance, which melts at 121°. It closely resembles conine in its chief properties, and may be converted into this alkaloid by reduction with hydriodic acid.

Pseudo-conydrine $C_8H_{17}NO$, which is also found in hemlock, closely resembles conydrine. It is a crystalline, strongly basic substance; m.p. 100–102°; b.p. 229–231°. It is a secondary base, and forms crystalline salts. Its constitution has not yet been fully elucidated, but it is evidently analogous to that of conydrine (Ladenburg a. Adam, B. 24, 1671).

Buxine $C_{18}H_{21}NO_3$ is found in *Buxus sempervirens*, and is probably identical with the *bebeerine* contained in bebeeru bark (*Nectandra Rodiæi*), and probably also with the *pelosine* of *Cissampelos Pareira*. Amorphous; m.p. 198° (Fauré, J. Ph. [2] 16, 432; Maclagan, A. 48, 109; 55, 105; Wiggers, A. 33, 81; Bödecker, A. 69, 53).

Calabarine, *v. Eserine.*

Cevadilline *v. Veratrine and the veratrum alkaloids.*

Cevadine *v. Veratrine and the veratrum alkaloids.*

Chelidonine $C_{19}H_{19}NO_6$, or $C_{20}H_{19}NO_5$, is one of several alkaloids contained in *Chelidonium majus* (Probst, A. 29, 123; Will, A. 35, 113; Eykman, R. T. C. 3, 190; Henschke, Ar. Ph. [3] 26, 624; Selle, *ibid.* [3] 28, 441). This alkaloid is also found in *Stylophoron diphyllum* (Selle, Ar. Ph. [3] 28, 96) and in *Sanguinaria canadensis* (König, C. C. 1891, i. 321).

Choline $C_5H_{15}NO_2$ is an amine which has recently been found in several plants; in hops (Griess a. Harrow, C. J. 47, 208), in ipecacuanha (Kunz, Ar. Ph. [3] 25, 461), in *Scopola japonica* (Schmidt a. Henschke, Ar. Ph. [3] 26, 185), in areca nuts (Jahns, B. 23, 2972), &c. Choline has long been known as the decomposition product of a number of substances occurring in the animal organism (lecithin, bile-acids, &c.). It is a base which reacts with acids like ammonium hydroxide, the acid radicle taking the place of hydroxyl. Choline is the hydroxyethyl-trimethyl derivative of ammonium hydroxide ($N(C_2H_4OH)(CH_3)_3OH$); its chloride may be produced by the action of trimethylamine with ethylene chlorhydrin. *V.* also Schmidt (A. 267, 249).

Cinchonine *v. Quinine.*

Cinchonibine $C_{19}H_{22}N_2O$ is one of ten bases formed when cinchonine sulphate is heated with sulphuric acid (Jungfleisch, Bl. 49, 747), *v.* also *Cinchonine.*

Cinchonidine *v. Quinine.*

Cinchonamine $C_{19}H_{24}N_2O$ is contained in *Remijia purdieana.* Crystals; m.p. 184–185°. The salts are crystalline. The nitrate is remarkable in being nearly insoluble in dilute nitric acid (Arnaud, Bl. 41, 590; Hesse, A. 225, 218).

Cinchamidine or **Hydrocinchonidine**
$C_{19}H_{24}N_2O$
occurs in very small quantities in several species of cinchona. Crystals; m.p. 229–230°. The salts are crystalline (Hesse, A. 214, 1).

Codeïne *v. Morphine and the opium alkaloids.*

Cocaïne and the Coca Alkaloids.

The different varieties (truxillo, cusco, &c.) of *Erythroxylon coca* contain several closely related alkaloids, the principal being the crystalline *cocaïne* ($C_{17}H_{21}NO_4$), which was first obtained by Niemann in 1831. The only other crystalline alkaloid which has so far been obtained from these plants is *cinnamyl-cocaïne* ($C_{19}H_{23}NO_4$), which seems to exert a physiological action similar to that of cocaïne itself. It is distinguished from cocaïne by its higher melting-point (121°), and by yielding benzaldehyde (bitter almond oil) when oxidised with permanganate (Giesel, C. C. 1889, ii. 765; Liebermann, B. 21, 3372).

Besides these two crystalline alkaloids, a number of amorphous bases have been described, of which the most important is the so-called *amorphous cocaïne*, the *cocamine* of Hesse (Hesse, Ph. [3] 18, 71; Paul, Ph. [3] 18, 781). This alkaloid would appear to be identical with the *truxilline* or isatropyl-cocaïne ($C_{19}H_{23}NO_4$) of Liebermann, which is an isomeride of cinnamyl-cocaïne and a powerful poison (Liebermann, B. 21, 2342; 22, 680).

Another amorphous alkaloid has been isolated by Giesel (C. C. 1890, i. 718; Liebermann a. Giesel, B. 23, 508), and was at first thought by him to be methyl-cocaïne. It has since proved to be an isomeride of cocaïne ($C_{17}H_{21}NO_4$), from which it differs in certain respects, chiefly in being dextrorotatory. It appears to be identical with the *dextro-cocaïne* artificially prepared by Einhorn and Marquart (B. 23, 468, 979; Liebermann a. Giesel, B. 23, 926).

The volatile alkaloid *hygrine* obtained from coca leaves by Lossen (A. 133, 352) is stated by Liebermann (B. 22, 675) to consist of two liquid bases. One is an isomeride of tropine ($C_8H_{15}NO$). It boils at 193–195°. The other, which does not distil under ordinary pressure without decomposition, is represented by the formula $C_{14}H_{24}N_2O$. Hesse, however, asserts that no such alkaloid as hygrine exists in coca leaves (Ph. 3, 21, 1132).

In addition to these bases, *benzoyl-ecgonine* ($C_{16}H_{19}NO_4$), one of the products of the hydrolysis of cocaine, has been found in coca leaves (Merck, B. 18, 2952); Liebermann (B. 24, 2336) has recently obtained yet another alkaloid from Java coca leaves, which is a tropeïne (*v. Atropine*), the *benzoyl-pseudo-tropeïne.* It is an oil which crystallises on standing; m.p. 49°. This alkaloid is strongly alkaline, optically inactive, and is dissolved by the ordinary solvents. It is monacidic; the *hydrochloride* is crystalline. The *aurichloride* forms fine crystals, which melt at 208°. On hydrolysis with hydrochloric acid, benzoyl-pseudo-tropeïne furnishes benzoic acid and pseudo-tropine, in most respects identical with the pseudo-tropine derived from hyoscine, but apparently differing from it in furnishing an aurichloride melting 27° higher than the point (198°) recorded by Ladenburg as the melting-point of the aurichloride of this base (Hesse, A. 271, 208). By acting on pseudo-tropine with benzoic anhydride Liebermann has reproduced benzoyl-pseudo-tropeïne.

The alkaloids *cocaïne, isatropyl-cocaïne, cinnamyl-cocaïne* are all derivatives of one and the same substance, viz. ecgonine, into which they are converted on hydrolysis. The three alkaloids differ only in respect of the acid group they contain. Ecgonine is closely related to tropine, of which the atropaceous alkaloids are derivatives (*v. Atropine*).

Cocaïne $C_{17}H_{21}NO_4$ occurs to a variable extent in the different varieties of coca leaves. The total alkaloid present in good commercial specimens amounts to about 1 p.c., of which from one-fourth to one-half is usually cocaïne (Hesse, Ph. [3] 21, 1109).

Preparation.—In extracting cocaïne from coca leaves great care has to be taken to avoid prolonged heating of the products with alkalis, acids, or even with water or alcohol, since the alkaloid very readily suffers hydrolysis. The following method is a slight modification of that used by Lossen (A. 133, 351). The coca leaves are exhausted by maceration and percolation with water having a temperature of 60–80°. The aqueous solution is precipitated with lead acetate, and the filtrate, after having been freed from lead by the addition of sodium sulphate, is somewhat concentrated. Ammonia is then added in slight excess, and the cocaïne extracted from the liquid by repeated agitation with ether. The cocaïne is purified either by crystallisation from alcohol, or by conversion into the hydrochloride, which is repeatedly crystallised, the regenerated alkaloid being crystallised from alcohol.

Another plan is to exhaust the leaves with ether, and to mix the residue left by the evaporation of the ether with magnesia and water, and thoroughly dry the paste. The powdered mass is then extracted with ether or amyl alcohol, and the alkaloid obtained by the evaporation of the ether or removed from the amyl alcohol by shaking with acid. It is then converted into hydrochloride, and the cocaïne regenerated from the recrystallised salt. The alkaloid is finally crystallised from alcohol.

Properties.—Monoclinic prisms; m.p. 98°; at higher temperatures it sublimes, with decomposition. Lævorotatory (Antrick, B. 20, 321); slightly soluble in cold water, more soluble in hot water. Readily soluble in alcohol, ether, benzene, light and heavy petroleum, and in carbon disulphide. The aqueous solution is alkaline to litmus, has a bitter taste, and produces a tingling and numbness of the tongue and lips, or, more generally, local anæsthesia of the surface to which it is applied. On this account it has been somewhat largely employed in minor surgical operations. The alkaloid also causes dilatation of the pupil of the eye, but is not so powerfully mydriatic as some of the solanaceous alkaloids. When administered internally in small doses, it acts as a stimulant, and diminishes the feeling of fatigue consequent on muscular exertion. The coca leaves have long been known to possess this property, and in places where the plant is abundant a mixture of lime and coca leaves is chewed by the natives before engaging in severe exertion. Larger doses of the alkaloid are poisonous.

The ordinary salts of cocaïne are crystalline. The *hydrochloride* $\bar{B}.HCl$, which is used in medicine as well as the alkaloid, crystallises anhydrous from alcohol, or with $2H_2O$ from water.

The chromate ($\bar{B}.H_2CrO_4.H_2O$) is thrown down as a pale-yellow amorphous precipitate when potassium chromate is added to an acid solution of the hydrochloride. This salt is very slightly soluble in cold water; m.p. 127°.

The *aurichloride* $B.HAuCl_4$ is crystalline, and sparingly soluble in water. When aqueous mercuric chloride is mixed with a solution of cocaïne hydrochloride, a bulky precipitate of the *mercurichloride* ($\bar{B}.HCl.HgCl_2,2H_2O$) is formed. This salt may be crystallised from alcohol; m.p. 124° (Müller, C. C. 1890, ii. 818).

Reactions and constitution.—Cocaïne exhibits most of the general reactions of the vegetable alkaloids. Like atropine, the free alkaloid precipitates mercuric oxide from an alcoholic solution of mercuric chloride. The formation of the chromate and mercurichloride are useful tests. When boiled with water cocaïne is gradually hydrolysed into *methyl alcohol* and *benzoyl-ecgonine*

$$C_{17}H_{21}NO_4 + H_2O \quad C_{16}H_{19}NO_4 + CH_3OH$$

(Paul, Ph. [3] 18, 781; Einhorn, B. 21, 47), and the same change gradually occurs if the alkaloid remains in contact with an alkaline liquid. Benzoyl-ecgonine, which is also found in coca leaves, crystallises from water with $4H_2O$. It is more soluble in water than cocaïne, and almost insoluble in ether. Its ordinary salts are crystalline. Benzoyl-ecgonine may be reconverted into cocaïne by heating with methyl iodide and a solution of soda in methyl alcohol (Merck, B. 18, 2264, 2952; Skraup, M. 6, 556), or more readily by passing hydrochloric acid gas into a solution of benzoyl-ecgonine in methyl alcohol (Einhorn, B. 21, 47). When cocaïne is heated with alkalis or mineral acids, methyl alcohol and benzoyl-ecgonine are first formed, but the latter undergoes further hydrolysis into *benzoic acid* and *ecgonine*:

$$C_{17}H_{21}NO_4 + 2H_2O$$
$$= CH_3OH + C_7H_6O_2 + C_9H_{15}NO_3.$$

Ecgonine ($C_9H_{15}NO_3$) crystallises from water with $1H_2O$; m.p. 198°. It is very soluble in water, sparingly so in alcohol, and insoluble in ether. It is neutral in reaction, and possesses both basic and acid properties; well characterised salts are formed by its union with acids and alkalis.

When heated with sulphuric acid ecgonine loses the elements of a molecule of water, furnishing *anhydro-ecgonine* ($C_9H_{13}NO_2$), and this base when heated with hydrochloric acid loses carbon dioxide and furnishes *tropidine* identical with that obtained from atropine (Einhorn, B. 23, 1338). When the crystalline barium salt of ecgonine is distilled it behaves like the salt of an organic acid, carbon dioxide being split off, whilst there distils over a liquid base *iso-tropine*, an isomeride of tropine. It boils at about 220°. By the further action of baryta iso-tropine furnishes methylamine (Merck, B. 19, 3002). On oxidation iso-tropine yields, amongst other products, succinic acid.

These reactions, as well as others which have been studied, go to prove that cocaïne, like atropine, is a derivative of tetrahydro-pyridine. Anhydro-ecgonine seems to be acrylic acid, into which the methyl-tetra-hydropyridine group has been introduced. When this compound takes up a molecule of water to form ecgonine, the elements of the water enter into the acrylic group, which becomes an hydroxypropionic group, the presence of carboxyl in which serves to explain the acid properties of ecgonine. In benzoyl-ecgonine the benzoic radicle has replaced the alcoholic hydrogen of the hydroxypropionic group. Cocaïne is the methyl ester of benzoyl-ecgonine $CH_2(CH_3NC_5H_7)CH.O(C_6H_5CO)CO.OCH_3$ (Einhorn, B. 20, 1221; 21, 47; 23, 1338). By the action of the various alkyl iodides and alcohols on benzoyl-ecgonine, homologues of cocaïne may be obtained which resemble cocaïne in chemical properties and in physiological action (Merck, B. 18, 2952; Novy, Ph. [3] 18, 233).

Since isatropyl-cocaïne and other amorphous alkaloids contained in coca leaves which are valueless for medicinal purposes yield ecgonine when heated with hydrochloric acid, it is worth while to convert them into this base and from it to prepare cocaïne by the reactions described above. Some of this artificial cocaïne is said to come into commerce (Liebermann a. Giesel, B. 21, 3196).

Detection and estimation of cocaïne.—Cocaïne may be detected by its characteristic action on the tongue, and also by the reactions mentioned above. In isolating it, the aqueous solution should not be heated for any length of time, and not at all in presence of acids or alkalis. For the liberation of the alkaloid from its salts, ammonia, and not fixed alkalis, should be employed.

For the estimation of the crystalline alkaloid (cocaïne and cinnamyl-cocaïne) in coca leaves, several processes have been recommended. The following method is said to afford accurate results. Fifty grms. of the powdered leaves are mixed with twenty grms. of magnesia, the mixture made into a paste with water, and dried at 60°. The finely powdered mass is exhausted with ether, the ether distilled, and the residue dissolved as far as possible in very dilute (2 p.c.) hydrochloric acid. The clear acid liquid is shaken with ether to remove colouring matter, excess of ammonia is added, and the alkaloid removed by repeatedly extracting with ether in the usual manner. The ethereal solution dried by calcium chloride is evaporated to dryness, and the residue weighed (Mark, P. Z. 1889, 349).

For the estimation of cocaïne in the crude alkaloid of commerce *v.* Squibb, Fr. 28, 743.

Colchicine $C_{22}H_{25}NO_6$, an alkaloid existing in the seeds of *Colchicum autumnale*; *v.* also COLCHICUM.

Properties.—A yellow varnish, soluble in water, alcohol, and chloroform. It unites with chloroform forming a crystalline compound ($\bar{B}.2CHCl_3$). Lævorotatory. The aqueous solution has a very bitter taste and is poisonous, its action resembling that of veratrine. The alkaloid dissolves in sulphuric acid, forming a yellow solution which becomes green, violet, and finally red on the addition of a drop of nitric acid. When heated with hydriodic acid, colchicine furnishes one molecular proportion of methyl iodide, together with *colchiceïne* ($C_{21}H_{23}NO_6$), an alkaloid which also occurs in *Colchicum autumnale*. When a solution of colchicïne is boiled with dilute sulphuric acid, colchiceïne and methyl alcohol are formed. Colchiceïne crystallises with $\frac{1}{2}H_2O$, and melts at 139°. It is lævorotatory, and has acid properties. Unlike colchicine, colchiceïne is not poisonous. Colchicine may be reproduced from colchiceïne by heating it with methyl iodide and a solution of soda in methyl alcohol (Zeisel, M. 7, 568; 9, 4, 868).

Conessine or **Wrightine** $C_{12}H_{20}N$? exists in *Wrightia antidysenterica* and in *Holarrhena africana*. Crystals; m.p. 122° (Polstorff, B. 19, 78, 1682; Warnecke, Ar. Ph. [3] 26, 248, 281; B. 19, 60).

Conydrine or **Conhydrine** *v. Conine.*

Corydaline $C_{18}H_{19}NO_4$ is found in the root of *Corydalis tuberosa*. Prismatic crystals, m.p. 130°. Insoluble in water, slightly soluble in alcohol, soluble in ether and chloroform. A diacidic base, which forms crystalline salts (Wicke, A. 137, 274). From the root of *Corydalis cava*, Adermann (C. C. 1891, 1, 978) has obtained an alkaloid resembling caffeïne, to which he assigns the formula $C_{22}H_{21}NO_4$ and names *corydaline*. The same plant contains *hydro-berberine* $C_{20}H_{21}NO_4$ (m.p. 138°), which is converted on oxidation into berberine.

Cupreine v. *Quinine.*

Curarine v. *Strychnine and the strychnos alkaloids.*

Cusconine $C_{23}H_{26}N_2O_4$, isomeric with aricine, which it accompanies in cusco bark. Crystals; m.p. 110° (Hesse, A. 185, 301).

Cusparine $C_{19}H_{17}NO_3$ or $C_{20}H_{19}NO_3$ is found in Angostura or Cusparia bark. Needle-shaped crystals; m.p. 92°. Sparingly soluble in ether, very soluble in alcohol (Körner a. Böhringer, G. 13, 363; Beckürts a. Nehring, Ar. Ph. 229, 591). See also CUSPARIA BARK.

Cytisine $C_{11}H_{14}N_2O$ is contained in laburnum (*Cytisus Laburnum*) (Husemann, Z. 1869, 677; Partheil, B. 23, 3201; 24, 634; Buchka a. Magalhaes, *ibid.* 24, 253, 674). Crystals; m.p. 153°, which sublime without decomposition. Soluble in water, alcohol, and chloroform, insoluble in light petroleum. Cytisine is a diacidic base whose salts are crystalline. The *aurichloride* $\bar{B}.HAuCl_4$ melts at 213°. According to Moer and Plugge (Ar. Ph. [2] 29, 48), cytisine should be represented by the formula $C_{11}H_{16}N_2O$. In aqueous solution it is lævorotatory $[\alpha]_D = -120°$, and gives with ferric chloride a red colouration, which is discharged by a few drops of aqueous hydrogen peroxide, a blue colouration being subsequently observed. Cytisine is a violent poison. This alkaloid is identical with *ulexine* (*q. v.*). According to Plugge (Ar. Ph. 229, 561), *sophorine*, the alkaloid of *Sophora tomentosa*, is identical with cytisine.

Delphinine $C_{22}H_{35}NO_6$ or $C_{62}H_{49}O_{14}$ and *Delphinoidine* $C_{50}H_{42}NO_8$ are found in the seeds of *Delphinium Staphisagria* (Lassaigne, A. Ch. [2] 12, 358; Couerbe, *ibid.* [2] 52, 359; Marquis, P. Z. 16, 449, 481, 513; Charalampi, P. Z. 29, 641).

Emetine $C_{30}H_{40}N_2O_5$? the alkaloid existing in ipecacuanha root (*Cephaëlis Ipecacuanha*), which contains between 1–2 p.c. (*v.* also IPECACUANHA).

Preparation.—The emetine may be extracted from ipecacuanha by mixing the finely powdered root with an equal weight of lime, and making the mixture into a paste with water. The mass, dried at 100°, is extracted with boiling chloroform, which dissolves the emetine.

Properties.—Crystals; m.p. 62–65°. Slightly soluble in water, more soluble in alcohol, chloroform, and benzene. Emetine is a diacidic base, and a tertiary diamine. When administered even in minute quantities it acts as a powerful emetic. For further information see Lefort (J. Ph. [4]

9, 241), Podwyszotsky (Ph. [3] 10, 642), Kunz (Ar. Ph. [3] 25, 461).

Estimation of emetine in ipecacuanha.—The estimation of emetine in ipecacuanha is best accomplished, according to Flückiger, by extracting the finely powdered root with boiling chloroform to which about 1 p.c. of aqueous ammonia has been added. The residue left on the evaporation of the chloroform is nearly pure emetine. Ransom finds that it is better to exhaust the root with chloroform made alkaline with ammonia by shaking with aqueous ammonia and then withdrawing the layer of water. The solution in chloroform is shaken with dilute sulphuric acid, and the quantity of emetine in the acid solution determined by titration with Mayer's solution (Ph. [3] 18, 241; *v.* also Kremel, Ar. Ph. [3] 26, 419).

Ergotinine $C_{35}H_{40}N_4O_6$ is found in ergot of rye (Tanret, A. Ch. [5] 17, 493), which also contains *cosmetine* (Bombelon, P. Z. 33, 109).

Eserine or **Physostigmine** $C_{15}H_{21}N_3O_2$, the alkaloid of Calabar bean (*Physostigma Venenosum*).

Preparation.—The powdered beans are extracted with alcohol and the alcohol distilled off, or the medicinal alcoholic extract may be used. The extract is mixed with excess of sodium bicarbonate and extracted with ether, the ethereal solution is shaken with dilute sulphuric acid, the acid liquid filtered, mixed with excess of sodium bicarbonate, and extracted with ether, which leaves the eserine (Jobst a. Hesse, A. 129, 115; Hesse, A. 141, 82).

Properties.—The alkaloid forms a varnish which is very slightly soluble in water, but readily soluble in alcohol, ether, and benzene. Strongly alkaline; forms salts with acids, the hydrobromide being crystalline (Duquesnel, Ph. [3] 5, 847). Lævorotatory. Causes contraction of the pupil of the eye—*i.e.* myotic—and when administered internally acts as a powerful poison. Decomposed by boiling with dilute acids. Is oxidised when exposed to air, especially in presence of alkali, forming a red crystalline colouring matter, *rubreserine.* When calcium chloride is added to its aqueous solution a fine red colouring matter is also produced. When alkalis act on eserine, the alkaloid *calabarine* appears to be formed (Harnach a. Wittkowski). It is doubtful whether this alkaloid actually exists in the Calabar bean, or is only produced during the extraction of the alkaloid by the decomposition of eserine. It has been found in specimens of the medicinal extract of Calabar bean which have been kept for some time. Its physiological action is antagonistic to that of eserine (Harnack a. Wittkowski, Arch. Exp. Path. 5, 401; 8, 125; 9, 434; 10, 301; 12, 101).

Gelsemine $C_{22}H_{38}N_2O_4$? an alkaloid occurring in the root of the American wild jasmine, *Gelsemium sempervirens.* In certain respects it resembles strychnine (Wormley, Ph. [3] 13, 106; Robbins, B. 9, 1182; Gerrard, Ph. [3] 13, 502, 641; Thompson, Ph. [3] 17, 803).

Properties.—Crystallises with difficulty from its alcoholic solution; m.p. 45°. Slightly soluble in water; readily soluble in alcohol, chloroform, and ether. The aqueous solution is strongly alkaline, and has a very bitter taste. It acts as a monacidic base; the principal salts are crystalline. When a crystal of potassium bichromate is introduced into a solution of gelsemine in strong sulphuric acid, a brilliant play of colours, passing from red and violet to green, is observed, which closely resembles that exhibited by strychnine. Unlike strychnine, however, it dissolves in sulphuric acid, forming a green solution which turns red (Dragendorff, Zeits. Anal. Chem. 22, 153; Raimondi, *ibid.* 26, 743). Gelsemine and its salts exert a mydriatic action on the eye, and when administered internally are highly poisonous.

Grandiflorine, a poisonous alkaloid contained in *Solanum grandiflora* (Freire, C. R. 105, 1074).

Harmaline $C_{13}H_{14}N_2O$, an alkaloid existing as phosphate in the seeds of *Peganum harmala* (Fritzsche, A. 64, 360; Göbel, A. 38, 363); *v.* also HARMALA.

Properties.—Small tabular crystals; m.p. 238°, with decomposition. Very slightly soluble in water, more soluble in alcohol and ether. A monacidic base; the salts are yellow, and their aqueous solutions exhibit a blue fluorescence. Heated with hydrochloric acid, harmaline furnishes *methyl chloride* and *harmalol.*

On oxidation harmaline is converted by loss of two atoms of hydrogen into *harmine* ($C_{13}H_{12}N_2O$), which is also found in small quantity in peganum seeds. Harmine is a crystalline alkaloid, m.p. 256°. Soluble in water, less soluble in alcohol than harmaline. The salts of harmine are colourless, in aqueous solution they show a blue fluorescence. When strongly heated with concentrated hydrochloric acid, harmine yields one molecular proportion of methyl chloride, together with harmol

$$(C_{12}H_{10}N_2O),$$

which has the properties of a phenol (Fritzsche a. Tauber, B. 18, 400; Fischer, B. 22, 637).

Oxidation with chromic acid converts harmine into harmic acid ($C_{10}H_8N_2O_4$).

Harmaline and harmine appear to be pyridine derivatives.

Homoquinine *v. Cupreïne.*

Hydrastine *v. Berberine and the berberis alkaloids.*

Hygrine *v. Cocaïne and the coca alkaloids.*

Hymenodictyonine $C_{23}H_{10}N_2$ occurs in the bark of *Hymenodictyon excelsum.* Needle-shaped crystals; m.p. 66°. A diacidic base, forming uncrystalline salts. Hymenodictyonine is a tertiary diamine (Naylor, Ph. [3] 13, 187; 15, 195).

Hypoxanthine *v. Caffeïne.*

Hyoscyamine *v. Atropine and the solanaceous alkaloids.*

Hyoscine *v. Atropine and the solanaceous alkaloids.*

Jaborine *v. Pilocarpine.*

Lupinine $C_{21}H_{42}N_2O_2$, an alkaloid found in the seeds of *Lupinus luteus.*

Properties.—Rhombic crystals, m.p. 67–68°. Distils without decomposition in hydrogen at 255–257°. A diacidic base, which furnishes crystalline salts (Baumert, B. 14, 1150; 15, 1951; Hagen, A. 230, 370; Siebert, Ar. Ph. 229, 531; Soldani, *ibid.* 230, 16).

Lupinidine $C_8H_{15}N$, another alkaloid occurring in the same plant. A syrupy liquid, which rapidly oxidises in air. Forms crystalline salts

(Baumert, A. 224, 325; 225, 368; 227, 217). Lupinidine is a powerful poison, which acts like curarine.

Lycaconitine *v. Aconitine and the aconite alkaloids.*

Mandragorine $C_{17}H_{23}NO_3$? is obtained from mandragora or mandrake root. It resembles atropine and hyoscyamine in its principal properties. The base is a hygroscopic resinous mass, which melts at 77-79°. The chief salts are crystalline; the aurichloride $\bar{B}.HAuCl_4$ melts at 153-155°. Mandragorine is not converted into atropine by heating with alkalis. It possesses mydriatic properties (Ahrens, A. 251, 312; B. 22, 2159).

Myoctonine *v. Aconitine and the aconite alkaloids.*

MORPHINE AND THE OPIUM ALKALOIDS (*v.* also OPIUM).

Opium, the partially dried juice of the seed-capsules of *Papaver somniferum*, contains the salts (sulphates and meconates) of a number of closely related alkaloids; as many as twenty alkaloids have already been described (*v.* OPIUM). Kauder (Ar. Ph. 228, 419) has recently re-investigated the alkaloidal constituents of opium, and describes a new alkaloid *tritopine*. Only the more important of these alkaloids will be considered here, *viz.*: morphine $C_{17}H_{19}NO_3$; codeïne $C_{18}H_{21}NO_3$; thebaïne $C_{19}H_{21}NO_3$; papaverine $C_{20}H_{21}NO_4$; narcotine $C_{22}H_{23}NO_7$.

With the exception of morphine and narcotine, opium does not usually contain more than a total of 1 p.c. of the other alkaloids. For an account of the reactions of the chief opium alkaloids *v.* Plugge (Ar. Ph. [3] 25, 793).

Morphine $C_{17}H_{19}NO_3$ was the first known vegetable alkaloid. It was isolated from opium about the year 1807 by Sertürner. Morphine is contained in several plants belonging to the natural order *Papaveraceæ*, although not in the common poppy.

The amount of morphine present in opium varies in different species (Indian, Turkey, &c.) from 3 to 20 p.c. The British Pharmacopœia states that the dried opium intended for medicinal use should contain 10 p.c.

Preparation.—Since the morphine exists in opium in the form of two soluble salts (meconate and sulphate), extraction with water removes the whole of the alkaloid from the product. Several methods have been suggested for the separation of this alkaloid; that suggested by Mohr (A. 35, 119) answers well. About 20 grms. of opium are thrice extracted with about 60 c.c. of boiling water. The hot liquid is mixed with 5 grms. of lime suspended in a little water, and the mixture boiled for a few minutes. The liberated morphine dissolves in the alkaline liquid, whilst nearly the whole of the other alkaloids, as well as the meconate and some sulphate of calcium, are precipitated. The mixture is filtered, and the precipitate washed with hot water; the liquid is evaporated until it measures 40 c.c. and then filtered. To the solution is added 2 grms. of ammonium chloride, which precipitates the morphine, since this alkaloid is but very slightly soluble in aqueous ammonia. The liquid is heated to expel all the ammonia, and allowed to stand for some hours. The morphine is then filtered off, and purified by dissolving it in hydrochloric acid, adding lime to the hot solution of the hydrochloride, filtering, and precipitating the morphine with ammonium chloride. The alkaloid may be crystallised from hot amyl alcohol.

Gregory's method for the isolation of morphine from opium consists in extracting the substance with lukewarm water, mixing the liquid with excess of chalk, and evaporating to a small volume. Slight excess of calcium chloride is now added, the liquid diluted with water, and the precipitated resin, calcium meconate &c. filtered off. On concentrating the liquid the hydrochlorides of morphine and codeïne crystallise out. These are dissolved in water, the solution decolourised with charcoal, and decomposed with excess of ammonia, which precipitates only the morphine.

Properties.—Small rhombic crystals containing $1H_2O$, which is gradually lost at 100°, more rapidly at 120°. At higher temperatures (about 230°) morphine melts with some decomposition, and afterwards a part of the alkaloid sublimes, together with some of its decomposition products. Slightly soluble in water—1 in 10,000 at 10°; 1 in 5,000 at 20° (Chastaing, Bl. [2] 37, 477); more soluble in boiling water (1 in 500). Soluble in absolute alcohol (1·1 in 100 at 10°; 1 in 13 at b.p.), less so in aqueous alcohol (1 in 100 at 15°; 1 in 36 at b.p.). Less soluble in amyl alcohol (1 in 400 at 11°; 1·1 in 50 at 78°). Very slightly soluble or nearly insoluble in ether, benzene, chloroform, and light petroleum (Florio, G. 13, 496). Readily soluble in solutions of fixed alkalis, especially when warm; less soluble in aqueous ammonia (rel. dens. ·97) (1 in 177 at 15°). Lævorotatory in aqueous soda, $[\alpha]_D = -70{\cdot}23°$; more strongly lævorotatory in acid solution (Hesse, A. 176, 190).

Morphine is a strong base; its alcoholic solution is alkaline to litmus. Dilute acids readily dissolve morphine, and the salts are generally easy to crystallise. As a base morphine is monacidic. The hydrochloride $B.HCl,3H_2O$ is a well crystallised salt, soluble in water (1 in 24 at 15°), slightly soluble in alcohol (Hesse, A. 176, 189). The *platinichloride* ($\bar{B}.HCl,PtCl_4$) is crystalline. For a list of the principal salts *v.* MORPHINE in WATTS' DICTIONARY OF CHEMISTRY The alkaloid and its salts have a bitter taste, and when administered in small doses exert a powerful narcotic action; in larger doses they are poisonous.

Reactions.—Morphine exhibits several characteristic colour reactions.

Solution of ferric chloride (almost free from acid) produces with the alkaloid, and with neutral solutions of its salts, a deep-blue colouration which is discharged by strong acids. This reaction is characteristic, and delicate in neutral or nearly neutral solutions; it does not appear to be exhibited by any other commonly occurring vegetable alkaloid.

Strong sulphuric acid (quite free from nitric acid) does not colour morphine unless the mixture is warmed, when a brown colouration is produced.

Nitric acid dissolves the alkaloid, with the production of a deep-red colour. If the morphine is first dissolved in strong sulphuric acid and then a drop of nitric acid added, a carmine colouration is observed.

Morphine is a powerful reducing agent, converting ferric salts into ferrous salts, solution of potassium ferricyanide into potassium ferrocyanide, and precipitating the metals from solutions of silver nitrate, and gold and platinum chlorides. Since it reduces aqueous iodic acid, liberating iodine, this reaction is often utilised as a test for morphine, the iodine being detected in the usual manner. The salts of morphine also liberate iodine from aqueous iodic acid.

Morphine is a tertiary base, which combines with one mol. prop. of alkyl iodide.

Dibenzoyl and diacetyl derivatives of morphine have been prepared, whence it may be inferred that the alkaloid contains two hydroxyl groups (Wright, C. J. 27, 1031; Wright a. Beckett, C. J. 28, 15; Wright a. Rennie, C. J. 37, 610). One of these hydroxyl groups is probably attached to a benzene nucleus, since it has phenolic properties. Morphine dissolves in alkalis, forming metallic derivatives, in which one atom of hydrogen of the morphine is replaced by metals (Chastaing, C. R. 94, 44).

When morphine is heated with hydrochloric acid (25 p.c.) in a closed tube at 140–150°, a molecule of water is separated, and anhydromorphine ('apo-morphine') $C_{17}H_{17}NO_2$ is produced. It is isolated by adding sodium bicarbonate in excess to the acid liquid, and shaking with ether, which dissolves the 'apomorphine.' The free base has not been crystallised; it is very unstable when exposed to air, absorbing oxygen, especially in presence of alkali, with the production of a green, and afterwards a red, colour. Unlike morphine, this alkaloid is soluble in cold water. The *hydrochloride* of anhydro-morphine is crystalline, and is used in medicine. The properties of 'apomorphine' appear to show that the base still contains the phenolic hydroxyl which is present in morphine. Its physiological action differs entirely from that of morphine, since it produces no narcotic effect, but acts as a powerful emetic (Matthiesen a. Wright, Pr. 17, 455; Marmé, Fr. 24, 643).

Alkaline solutions of morphine absorb oxygen from the air, which converts the morphine by removal of two atoms of hydrogen into *pseudo-morphine* $C_{17}H_{17}NO_3$, a base which also results from the action of weak oxidising agents on morphine, and is found in small quantity in opium (Hesse, A. 141, 87; Suppl. 8, 267; A. 222, 234).

Picric acid is formed when morphine is oxidised with fuming nitric acid. Nitrous acid produces a nitroso- derivative. When morphine is distilled over hot zinc-dust, a large quantity of the hydrocarbon *phenanthrene* ($C_{14}H_{10}$) is obtained, together with *phenanthrene-quinoline* $C_{17}H_{11}N$, *pyridine*, and other substances (Gerichten a. Schrötter, A. 210, 396).

When heated with potash, morphine furnishes *methylamine*, together with other substances, amongst them being *protocatechuic acid* (Wertheim, A. 73, 208; Barth, M. 4, 70). According to Skraup and Wiegmann (M. 10, 110), ethyl-methylamine is obtained by the action of alcoholic potash on morphine. Very little can at present be stated with certainty as to the precise constitution of morphine. It seems likely that it is a derivative of phenanthrene-quinoline (Gerichten a. Schrötter, *l.c.*; Knorr, B. 22, 1113).

Detection and estimation.—Morphine affords precipitates with most of the alkaloidal reagents. It may be identified by means of the properties and reactions described above. The characteristic reactions of morphine can, however, only be relied on, when a nearly pure alkaloid has been experimented with. Unfortunately, morphine is one of the most difficult alkaloids to separate from much organic impurity, especially when it is present only in minute quantity, as is generally the case in toxicology. Since the internal administration of opium, and not of morphine itself, is usually the cause of poisoning, the existence of this alkaloid may be confirmed by detecting meconic acid, which is easy to recognise, and as it does not occur in any other substance is satisfactory proof of the presence of opium.

For a detailed account of the qualitative reactions of morphine *v.* Marmé, *l.c.*

For the estimation of the quantity of morphine in opium, several methods have been proposed. The accuracy of these methods has been compared by Venturini (G. 16, 239), who recommends Flückiger's process (Ar. Ph. [3] 27; 721, 769), which is as follows: 8 grms. of powdered opium dried at 100° are washed on the filter with a mixture of 10 c.c. of ether and 10 c.c. of chloroform, in order to remove narcotine. The opium is then washed with 10 c.c. more chloroform, and dried. It is then digested with 80 grms. of water at 25°C., with frequent shaking for twelve hours. The mixture is filtered, and 42·5 grms. of the filtrate (equal to 4 grms. of opium) are mixed in a small flask with 7·5 c.c. of alcohol (rel. dens. ·832), 15 c.c. of ether, and 1 c.c. of aqueous ammonia (rel. dens. ·960). The flask is stoppered, and allowed to remain for about twelve hours at about 5°, the mixture being frequently shaken. The morphine crystallises out of the ethereal layer, which is separated, and the morphine washed with 10 c.c. of water. The crystals are collected, and dried at 100°. Since some of the morphine crystallises on the sides of the flask and is difficult to remove, the alkaloid may be weighed in the flask instead of on the filter.

The British Pharmacopœia (1885) adopts the following method: 9 grms. (140 grains) of powdered opium dried at 100° are mixed with 4 grms. (60 grains) of slaked lime, and stirred in a mortar with 25·8 c.c. of water (400 grain-measures). The mixture is then diluted with 64·5 c.c. of water (1,000 grain-measures), and occasionally stirred during about half an hour. The mixture is then filtered into a stoppered bottle, until a volume of 67·1 c.c. (1,040 grain-measures) representing 6·45 grms. (100 grains) of opium has been obtained. To this filtrate 7·1 c.c. of alcohol (110 grain-measures) are added, and 32·2 c.c. of ether (500 grain-measures), and the mixture well shaken. In order to precipitate the morphine from its solution in the lime-water, 2·58 grms. of ammonium chloride (40 grains) are added, and the mixture well shaken. After the lapse of twelve hours the morphine will have crystallised out. Decant the ethereal layer, and filter it through a small counterbalanced paper. Add 12·9 c.c. (200 grain-measures) of ether to the contents of the bottle, gently shake, again decant and filter the ethereal layer. Wash the filter paper with 6·45 c.c. (100 grain-measures) of ether, and dry it. Now filter off the crystals which remain in the bottle, using about 13 c.c. of water for washing. The crystals of morphine are dried at 100° and weighed. Teschemacher and Smith (C. N. 35, 47; 57, 93, 103) claim to have devised a method by means of which more morphine is isolated than by any other.

For an account of the different methods which have been proposed *v.* Prescott's Organic Analysis.

For the estimation of morphine in tincture of opium (laudanum), the following method is said to afford accurate results: 75 c.c. of the laudanum are evaporated to dryness on the water-bath, and the residue thoroughly mixed with 75 c.c. of water and 2 grms. of calcium hydroxide. The liquid is then filtered, and 50 c.c. of the filtrate (representing the same quantity of laudanum) are mixed with 5 c.c. of alcohol, 25 c.c. of ether, and 3 grms. of ammonium chloride. The mixture is well shaken, and allowed to remain for twelve hours. The crystals of morphine, which will have separated, are collected, washed with water, dried at 60°, and weighed. The percentage of morphine is obtained by multiplying the weight of the crystals by two, and by the relative density of the tincture.

Codeïne or *Methyl Morphine* $C_{18}H_{21}NO_3$ exists in small quantity in opium (·1–1 p.c.).

Preparation.—The mixed hydrochlorides of morphine and codeïne having been separated from opium by Gregory's method (*v. Morphine*), and the morphine precipitated by ammonia, the alkaline filtrate, which contains codeïne hydrochloride, is evaporated to a small volume and precipitated by potash. The codeïne is purified by crystallisation from ether or from water. Codeïne may be prepared from morphine by heating it with alcoholic soda and methyl iodide (Grimaux, A. Ch. [5] 27, 273; Hesse, A. 222, 210).

Properties.—Large rhombic crystals (from water) with $1H_2O$, which melt in boiling water; small anhydrous crystals from ether, m.p. 153°. Lævorotatory. Slightly soluble in cold water, more soluble in hot water, alcohol, ether, and benzene; insoluble in light petroleum. The aqueous solution is strongly alkaline. Codeïne is a monacidic base; the principal salts are crystalline, and soluble in water. The physiological action of codeïne and its salts is similar to that of morphine.

Reactions and constitution.—Codeïne is distinguished from morphine by not giving the colour reaction with ferric chloride, and by producing with nitric acid a yellow, and not a red, colour. Concentrated sulphuric acid does not colour codeïne except after prolonged standing, but if a trace of nitric acid or ferric salt is added to the mixture it becomes blue. For an account of the qualitative reactions of codeïne *v.* Marmé, Fr. 24, 643. The decomposition products of codeïnes are, for the most part, analogous to those of morphine, of which it is the methyl derivative. The methyl group replaces an atom of hydrogen in one of the hydroxyl groups of morphine, probably in the phenolic group since codeïne has not the acid properties of a phenol. Codeïne, therefore, contains a methoxyl group, the presence of which may be ascertained by heating the alkaloid with hydrochloric acid, when methyl chloride is obtained. Codeïne may be prepared from morphine, the methyl group being introduced in the usual manner (*v. supra*).

Thebaïne $C_{19}H_{21}NO_3$ occurs in small quantity in opium. For the method of isolating it *v.* Hesse, A. Suppl. 8, 262.

Properties and reactions.—Leafy or prismatic crystals; m.p. 193°. Lævorotatory. Nearly insoluble in cold water, slightly soluble in ether, very soluble in alcohol, chloroform, and benzene. Slightly soluble in aqueous alkalis. Thebaïne is a monacidic base; the principal salts are crystalline, and soluble in water. The alkaloid and its salts are very poisonous. Thebaïne is coloured bright red by concentrated sulphuric acid. It is converted into its isomeride *thebenine* when warmed with dilute acids, and by the action of concentrated sulphuric acid is converted into another isomeride *thebaïcine.* Thebaine is attacked by concentrated hydrochloric acid, with the formation of two molecular proportions of methyl chloride and a base *morpho-thebaïne*

$$C_{17}H_{15}NO(OH)_2.$$

Thebaïne, therefore, contains two methoxyl groups (Howard a. Roser, B. 19, 1596).

Papaverine $C_{20}H_{21}NO_4$. For the method of isolating this alkaloid from opium *v.* Hesse, A. 153, 75; A. Suppl. 8, 289.

Properties.—Prismatic crystals; m.p. 147°. Very slightly soluble in hot and cold water; easily soluble in alcohol, chloroform, and benzene. Optically inactive. A monacidic base, which forms crystalline salts.

Reactions and constitution.—Sulphuric acid dissolves papaverine in the cold without colouration, but on warming the solution becómes dark violet.

Benzoic and acetic anhydrides do not react with papaverine, which consequently does not contain hydroxyl.

Nascent hydrogen converts papaverine into a *tetrahydride.*

When heated with concentrated hydriodic acid papaverine furnishes *papaveroline*

$$C_{16}H_{13}NO_4,$$

together with four molecular proportions of methyl iodide, from which it is inferred that four methoxyl groups are present.

By the action of hydrochloric acid, methyl chloride is obtained, together with some *homopyrocatechol* ($C_6H_3(CH_3)OH)_2$).

On oxidation with permanganate, papaverine yields a large number of products, the principal being *veratric acid*, *meta-hemipinic* or *dimethoxy- ortho-phthalic acid*

$$(C_6H_2(OCH_3)_2(CO_2H)_2,$$

pyridine-α-tricarboxylic acid, and *meconine* and *papaveraldine.*

When fused with alkali, papaverine affords *veratric acid*, together with *dimethoxyl-quinoline.*

From these and other results, Goldschmiedt (M. 4, 704 and following volumes) has concluded that papaverine is the tetra-methoxyl derivative of tolyl-isoquinoline (M. 9, 349). The alkaloids narcotine, hydrastine, and berberine have been shown to possess a very similar structure, and also the rare opium alkaloid *cryptopine* (Perkin, C. S. Proc. 1891, 166).

Narcotine $C_{22}H_{23}NO_7$ usually occurs to the extent of about 1 p.c. in opium, but sometimes in larger quantity. Unlike the majority of alkaloids, narcotine appears, as a rule, to exist in the plant for the most part as the free alkaloid, and not as a salt.

Preparation.—If opium is extracted with water in order to isolate the morphine &c., the greater part of the narcotine usually remains undissolved, since this alkaloid is nearly insoluble in water. By exhausting the residue with dilute hydrochloric acid, the narcotine is removed as hydrochloride, and from the solution of this salt the base may be precipitated by sodium bicarbonate, and crystallised from alcohol. Or the narcotine may be extracted from the opium by boiling it with ether; *v.* also Hesse, A. Suppl. 8, 284.

Properties.—Prismatic crystals; m.p. 176°. Almost insoluble in water (1 in 25,000 at 15°; 1 in 7,000 at 100°); soluble in alcohol (1 in 100 at 15°; 1 in 20 at b.p.); soluble in ether (1 in 166 at 16°); and in benzene (1 in 22 at 15°); very soluble in chloroform (1 in 2·69 at 15°); slightly soluble in amyl alcohol and in light petroleum. Dissolves in lime and baryta water, and slightly in aqueous ammonia. Lævorotatory, $[\alpha]_D = -185°$ in alcohol (Hesse, A. 176, 192). The solution in dilute acids is dextrorotatory. Narcotine is a feeble monacidic base; its aqueous solution is neutral to litmus. The principal salts crystallise with difficulty; their aqueous solutions are acid, and are decomposed, with separation of narcotine when evaporated. The free alkaloid may even be extracted from the aqueous solutions of some narcotine salts by agitating with ether or chloroform. In larger doses than are necessary in the case of morphine, narcotine and its salts exert a narcotic action.

Reactions.—Concentrated sulphuric acid dissolves narcotine, and the solution soon becomes yellow; on warming, a rapid transition of different colours is observed, the mixture becoming orange-red, blue, and finally purple. Nitric acid dissolves the alkaloid, with a yellow colour.

Narcotine is a tertiary base. It does not react with benzoic or acetic anhydrides, and therefore does not contain hydroxyl. When heated with water in a closed tube at 100°, or by prolonged ebullition with water, it is resolved into *opianic acid* and *hydrocotarnine*

$$C_{22}H_{23}NO_7 + H_2O = C_{10}H_{10}O_5 + C_{12}H_{15}NO_3$$

(Beckett a. Wright, C. J. 28, 583).

When heated with hydriodic acid, narcotine furnishes three molecular proportions of methyl iodide, together with the base *nornarcotine* ($C_{19}H_{17}NO_7$ or $C_{19}H_{11}(OH)_3NO_4$). The less energetic action of hydriodic acid produces one molecular proportion of methyl iodide, and *dimethyl-nornarcotine* $C_{19}H_{11}(OCH_3)_2(OH)NO_4$, or two molecular proportions of methyl iodide and *methyl-nornarcotine* $C_{19}H_{14}(OCH_3)(OH)_2NO_4$. *Methylamine*, together with meconine, is formed when narcotine is boiled with baryta water, or, if concentrated aqueous potash is used, *trimethylamine* is produced.

Nascent hydrogen converts narcotine into *meconine* (the reduction product of opianic acid) and *hydrocotarnine* ($C_{12}H_{15}NO_3$). On oxidation narcotine furnishes *cotarnine* ($C_{12}H_{15}NO_4$) and *opianic acid* ($C_6H_2(OCH_3)_2CHO.COOH$), which on further oxidation becomes hemipinic acid

$$C_6H_2(OCH_3)_2(COOH)_2.$$

When dilute nitric acid is used to oxidise, a series of products is obtained by oxidation of the cotarnine and meconine first formed by hydrolysis, viz. *apophyllic acid* ($C_8H_7NO_4$), *opianic acid*, and *hemipinic acid* ($C_6H_2(OCH_3)_2(COOH)_2$), this last acid being isomeric with the meta-hemipinic acid obtained by the oxidation of papaverine (Goldschmiedt, M. 9, 762).

There can be no doubt that narcotine is composed of a residue of cotarnine and of opianic acid. Cotarnine on oxidation furnishes apophyllic acid, which seems to be the methyl betaine of cinchomeronic acid (pyridine dicarboxylic acid); it is also obtained by the oxidation of cinchonine (*v. Quinine and the cinchona alkaloids*). Cotarnine and opianic acid, as indicated above, are benzene derivatives. The exact constitution of cotarnine, as well as the mode in which its residue is united to that of opianic acid in the molecule of narcotine, is not yet fully established. It seems probable, however, that cotarnine is the methoxyl derivative of hydrastinine, and narcotine the methoxyl derivative of hydrastine (*v. Berberine and the berberis alkaloids*), in which case the nucleus (probably iso-quinoline) of these alkaloids must be identical (Schmidt a. Wilhelm, Ar. Ph. [3] 26, 329; Roser, A. 249, 156, 168; 254, 334, 359).

Napelline. A name applied by Hübschmann to what was probably a mixture of amorphous alkaloids from *Aconitum Napellus*. *V. Aconitine and the aconite alkaloids.*

Nicotine $C_{10}H_{14}N_2$, a volatile alkaloid found as a salt (malate) in tobacco (*Nicotiana Tabacum*) and in the various species of *Nicotiana*. It is probable that this alkaloid also occurs in Indian hemp (*Cannabis Indica*) (Preobraschensky, P. Z. 1876, 705), and in the Australian plant 'pituri' (*Duboisia Hopwoodii*) (Liversidge, C. N. 43, 124; Petit, Ph. [3] 9, 819), but its presence in these two plants needs confirmation. Tobacco may contain from 1–8 p.c.; the common varieties contain from 1–4 p.c., the best samples containing the least nicotine.

Preparation.—Finely powdered tobacco leaves are exhausted either with boiling water or alcohol. The concentrated aqueous solution, or the residue left on the distillation of the alcohol, is mixed with a slight excess of lime or potash, and distilled in a current of steam. The distillate is made acid with oxalic acid, and evaporated to a syrup. This is mixed with ether, and then aqueous potash is gradually added to liberate the nicotine, which dissolves in the ether. The ether is removed, and the liquid extracted with more ether. The ethereal solution is distilled, and the residue of moisture is finally distilled off in a stream of hydrogen (Laiblin, A. 196, 130; Schlösing, A. Ch. [3] 19, 230).

Properties.—Pungent hygroscopic liquid, which oxidises on exposure to air, becoming brown and resinous; b.p. 247°. Distils without decomposition in a stream of hydrogen or amyl alcohol, but suffers oxidation when distilled in air. Rel. dens. 1·0110 at 20° (Landolt, A. 189, 318). Lævorotatory, $[\alpha]_D = -61·55$; salts, dextrorotatory. Mixes in all proportions with water, alcohol, and ether. Water also dissolves in nicotine with evolution of heat, forming what appears to be a hydrate, which crystallises when the solution is cooled. The aqueous solution of nicotine is strongly alkaline, and precipitates the solutions of many metallic salts. A diacidic base; most of the salts are crystalline, and contain the full proportion of acid. Nicotine and its salts are powerful poisons.

Reactions.—Nicotine or its salts are precipitated, even in dilute solutions, by the usual alkaloidal reagents. Concentrated sulphuric acid colours it red. Warm hydrochloric acid dissolves it with the production of a violet colour, and nitric acid with the formation of an orange colour.

In combining with alkyl iodides, nicotine behaves as a tertiary diamine.

Nascent hydrogen converts nicotine into a *hexahydride*. When its vapour is passed through a red-hot tube a number of homologous pyridine bases (pyridine, picoline, β-propyl pyridine, &c.) are obtained.

On oxidation nicotine furnishes nicotinic acid (β-pyridine carboxylic acid).

Nicotine is probably a di-pyridine, but its exact constitution is still uncertain (Cahours a. Etard, C. R. 88, 999; 90, 275; 92, 1079).

Oxy-acanthine *v. Berberine and the berberis alkaloids.*

Papaverine *v. Morphine and the opium alkaloids.*

Pelletierine $C_8H_{15}NO$ is a liquid alkaloid contained in pomegranate bark (*Punica Granatum*).

Properties.—Liquid; rel. dens. ·988 at 0°. Darkens and resinifies in air; b.p. 195°. Dextrorotatory. Soluble in water (1 in 20 at 15°); readily soluble in alcohol, ether, and chloroform. The aqueous solution is alkaline. The salts are crystalline.

Isopelletierine($C_8H_{15}NO$) and *methyl-pelletierine* ($C_9H_{17}NO$) are two liquid alkaloids, also found in pomegranate bark. *Pseudo-pelletierine* ($C_9H_{15}NO$) is a crystalline solid, m.p. 46°, found in the same plant. All these alkaloids are apparently nearly related (Tanret, Bl. 32, 464, 466; 36, 256).

Pelosine *v. Buxine.*

Physostigmine *v. Eserine.*

Pilocarpine $C_{11}H_{16}N_2O_2$, an alkaloid occurring in the leaves of jaborandi (*Pilocarpus pennatifolius*) and in other species of pilocarpus (Hardy, Bl. 24,497; Gerrard, Ph. [3] 5, 865, 965; Harnack a. Meyer, A. 204, 67); *v.* also JABORANDI.

Preparation.—The leaves are extracted with alcohol (84 p.c.) to which 1 p.c. of strong aqueous ammonia has been added in order to effect the liberation of the base from its salt. The solution is neutralised with tartaric acid, and the alcohol distilled. The residue is extracted with alcohol made alkaline with ammonia, the alcohol distilled from the clear liquid, and the pilocarpine extracted from the residue with chloroform. The impure alkaloid left on the evaporation of the chloroform is converted into the nitrate, and the salt crystallised from its solution in boiling alcohol. The pilocarpine may be obtained from the pure nitrate by decomposition with ammonia, and extraction of the aqueous solution with chloroform (Gerrard, Ph. [3] 7, 225; Poehl, B. 13, 2401).

Properties.—Crystals, easily soluble in water, alcohol, and chloroform, slightly soluble in ether. Dextrorotatory $[\alpha]_D = +101·6°$. Pilocarpine has acid as well as basic properties. It dissolves in aqueous alkalis, forming salts which are soluble in water and alcohol, but do not crystallise. They are decomposed by carbon dioxide, pilocarpine being regenerated.

The copper and silver salts are sparingly soluble in water. These compounds are the salts of the monobasic pilocarpic acid

$$(C_{11}H_{18}N_2O_3),$$

of which pilocarpine is the anhydride. The free acid is unknown (Hardy a. Calmels, Bl. 46, 479; 48, 221).

In combining with acids, pilocarpine acts as a monacidic base. The principal salts are crystalline.

Pilocarpine itself combines with platinum and gold chlorides, forming crystalline addition compounds. The usual *platinichloride* and *aurichloride* also exist (Hardy a. Calmels, Bl. 48, 220).

Pilocarpine and its salts are poisonous; they exert a myotic action—*i.e.* cause contraction of the pupil of the eyes—and also act, even in small doses, as sialogogues, producing a great increase of the flow of saliva.

Reactions.—When heated to 150° pilocarpine decomposes into *jaborine* ($C_{22}H_{32}N_4O_4$), *pilocarpidine* ($C_{10}H_{14}N_2O_2$), and *jaboric acid*

$$(C_{19}H_{25}N_2O_5)$$

(Hardy a. Calmels, Bl. 46, 479; 48, 225). Jaborine and pilocarpidine also occur in jaborandi leaves. The physiological action of pilocarpidine is similar to that of pilocarpine, but the action of jaborine is antagonistic to that of pilocarpine and resembles that of atropine.

Concentrated hydrochloric acid, when heated with pilocarpine, produces *methyl alcohol* and *pilocarpidine.*

When strongly heated with water in a closed tube, pilocarpine breaks up into *trimethylamine* and β-*pyridine* α-*lactic acid*

$$C_{11}H_{16}N_2O_2 + H_2O =$$
$$(CH_3)_3N + CH_3.C(C_5H_4N)OH.CO_2H.$$

Oxidation with permanganate converts pilocarpine into *trimethylamine*, *ammonia*, and *pyridine-tartronic acid*, which on further oxidation furnishes *nicotinic acid* (C_5H_4NCOOH) (β-pyridine carboxylic acid).

When barium pilocarpate is distilled, a new base *jabonine* $C_{19}H_{14}N_2$ is formed.

The constitution of pilocarpine has been elucidated, and its synthesis effected, by Hardy and Calmels (Bl. 48, 234; C. R. 105, 68). The principal steps are as follows: β-pyridine α-lactic acid ($CH_3.C(C_5H_4N)OH.CO_2H$) is converted into pilocarpidine by replacing its alcoholic hydroxyl by the residue of trimethylamine ($N(CH_3)_2$). In order to effect this change, the acid is heated with phosphorous bromide, which replaces the alcoholic hydroxyl by bromine, forming the corresponding pyridine bromopropionic acid ($CH_3C(C_5H_4N)BrCO_2H$). When this acid is heated with an aqueous solution of trimethylamine to 150°, methyl bromide is produced, together with pilocarpidine

$$(CH_3.C(C_5H_4N)N(CH_3)_2.CO_2H).$$

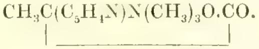
Pilocarpidine combines with one molecular proportion of methyl iodide, forming pilocarpidine methiodide ($CH_3.C(C_5H_4N.CH_3I)N(CH_3)_2.CO_2H$), in which the methyl iodide is attached to the nitrogen in the pyridine and not to that in the amine; this compound is therefore isomeric, and not identical with that which when decomposed with silver oxide would give pilocarpine. If, however, pilocarpidine is heated with methyl iodide and a solution of soda in methyl alcohol, a compound is obtained in which methyl iodide is attached to the nitrogen in the pyridine residue, and methyl alcohol is united with the nitrogen in the trimethylamine residue

$$(CH_3.C(C_5H_4N.CH_3I)N(CH_3)_2CH_3OH.CO_2H).$$

On oxidising this compound with silver permanganate, the methyl iodide only is attacked and converted into silver iodide and formic acid. The pilocarpic acid

$$(CH_3.C(C_5H_4N)N(CH_3)_3OH.COOH)$$

thus formed by the removal of the methyl iodide at once loses water, forming its betaïne-anhydride, pilocarpine



$$CH_3C(C_5H_4N)N(CH_3)_3O.CO.$$

Piperine $C_{17}H_{19}NO_3$, the alkaloid contained in *Piper nigrum* and in *P. album*, as well as in other plants belonging to the natural order *Piperaceæ*. Commercial black and white pepper contain from 5-9 p.c. of this alkaloid.

Preparation.—Piperine may be extracted from finely powdered pepper, preferably white pepper, by means of alcohol. The alcohol is distilled from the solution, and the alkaloid precipitated from the remaining aqueous residue by adding excess of potash, so that the greater part of the resin is dissolved. The base is purified by crystallisation from alcohol.

Another plan is to mix the powdered pepper with milk of lime, and boil the mixture for about fifteen minutes; it is then evaporated to dryness on the water-bath. The free piperine is extracted from the dry mass by means of boiling ether and crystallised from alcohol (Cazeneuve a. Caillot, Bl. [2] 27, 290).

Properties.—Monoclinic crystals; m.p. 128–129°. Slightly soluble in water, more soluble in ether, alcohol, benzene, and chloroform. Optically inactive. Piperine is a weak base. It is not alkaline, and does not dissolve in dilute acids. The principal salts are formed by combination with acids in the absence of much water. The *platinichloride* and *mercurichloride* are insoluble in water.

Reactions.—Piperine dissolves in strong sulphuric acid, forming a dark-red solution. Nitric acid converts the alkaloid into a resinous mass, which dissolves in potash, producing a dark-red solution.

When piperine is heated with aqueous alkalis, it is hydrolysed into a base *piperidine* and *piperic acid*

$$C_{17}H_{19}NO_3 + H_2O = C_5H_{11}N + C_{12}H_{10}O_4.$$

Piperidine is identical with the hexahydride of pyridine, whilst piperic acid is a paraffinic derivative of proto-catechuic acid

$$(C_6H_3(CH_2O_2)(CH)_4COOH).$$

Piperine has been prepared by the action of the chloride of piperic acid (piperyl chloride) on pyridine hexahydride (piperidine) (Rugheimer, B. 15, 1390). Piperine is thus proved to be piperyl piperidine; it is probable that the piperyl group is joined to the nitrogen of piperidine.

Piturine, the principal alkaloid contained in the Australian plant 'pituri' (*Duboisia Hopwoodii*), is probably identical with nicotine (*v. Nicotine*). This conclusion is supported by a comparison of the physiological action of the two alkaloids (Langley a. Dickenson, Journ. Physiol. 11, 265).

Protopine $C_{20}H_{17}NO_5$ is found in *Chelidonium majus*, *Sanguinaria canadensis*, and in very small quantity in opium. Crystals; m.p. 204°. The salts are crystalline; the *aurichloride* $B.HAuCl_4$ melts at 182° (Selle, Ar. Ph. 228, 441; König, C. C. 1891, i. 321).

Pseudaconitine *v. Aconitine and the aconite alkaloids.*

QUININE AND THE CINCHONA ALKALOIDS.

The barks of the different species of cinchona (*C. officinalis*, *C. succirubra*, *C. Ledgeriana*, *C. Calisaya*, &c., &c.) contain a large number of crystalline and amorphous alkaloids (*v.* CINCHONA BARK and CINCHONA BASES in WATTS' DICTIONARY OF CHEMISTRY, new edit., and Die Chinarinde by F. A. Flückiger, Eng. trans., 1884). These alkaloids exist in the bark chiefly as salts of quinic acid and cincho-tannic acid. Only the most important of these compounds will be dealt with here. The following are the names and formulæ of the principal cinchona alkaloids:

Quinine Quinidine or Conchinine	$C_{20}H_{24}N_2O_2$
Cinchonine Cinchonidine	$C_{19}H_{22}N_2O$
Quinamine Quinidamine or Cinchonamine	$C_{19}H_{24}N_2O_2$.

Cupreine $C_{19}H_{22}N_2O_2$ (from *China Cuprea* or *Remijia pedunculata*).

Quinine $C_{20}H_{24}N_2O_2$, the principal crystalline alkaloid contained in the bark (not in the wood) of many species of cinchona. The amount of quinine contained in the different species varies considerably.

C. Ledgeriana is said sometimes to contain as much as 11 p.c. of quinine, whilst *C. officinalis*, *C. Calisaya*, and *C. succirubra*, the common varieties, usually contain from 2–5 p.c. of quinine. The alkaloids which commonly accompany the quinine in these barks are cinchonidine, cinchonine, and quinidine, but the kind and quantity of the accompanying alkaloids vary in the different species.

Preparation.—The total alkaloids are first extracted from the bark. Water dissolves for the most part only the alkaloidal quinates, and not the cinchotannates. The cinchotannates may be dissolved by a dilute acid (sulphuric or hydrochloric acid), or they (as well as the quinates) may be decomposed, and the alkaloids liberated by mixing the bark with an aqueous alkali (lime and water). The various processes proposed for the extraction of the total alkaloid from cinchona bark involve the decomposition of the natural salts in one or other of these two ways. Extraction with dilute hydrochloric acid, which was at first largely resorted to, has been almost entirely abandoned, since much colouring matter is dissolved as well as alkaloid, and its complete removal complicated the subsequent operations. On the large scale the finely powdered bark is mixed with about one-third of its weight of slaked lime, and made into a paste with water. The mixture is thoroughly dried at 100°, powdered, and exhausted in an extraction apparatus with boiling petroleum (Landrin, C. R. 108, 750), alcohol, or amyl alcohol. On the small scale, chloroform, ether, or a mixture of three volumes of benzene with one of amyl alcohol may be employed. The alkaloids are removed from the solvent by agitating it (or, in the case of alcohol, the evaporated residue is similarly treated) with dilute hydrochloric acid, and the alkaloids are precipitated from the clear acid solution by a slight excess of soda or ammonia.

The alkaloids thus obtained from an ordinary commercial specimen of cinchona bark will, as a rule, be chiefly composed of quinine, cinchonidine, cinchonine, and a little quinidine.

A nearly complete separation of the quinine may be effected by taking advantage of the smaller solubility of quinine sulphate in cold water. The total alkaloid is dissolved in a slight excess of very dilute sulphuric acid, and almost, but not quite, exactly neutralised with dilute soda or ammonia. The solution is heated to 100°, and diluted with hot water, so that for each gram of total alkaloid taken there will be about 70 c.c. of solution. On cooling this solution to 15°, quinine sulphate will crystallise, whilst nearly the whole of the other alkaloidal sulphates will remain dissolved. The salt thus obtained is recrystallised several times from boiling water. Great care must be taken in the first instance not to leave the liquid more than just perceptibly acid, or the quinine sulphate will be converted into the exceedingly soluble acid sulphate. Hesse affirms that quinine sulphate may be entirely freed from small quantities of cinchonidine sulphate (which is the most difficult to remove) by two crystallisations from faintly acidulated water (Ph. [3] 15, 869; [3] 16, 818; *cf.* Davies, Ph. [3] 16, 358; Kerner, Ar. Ph. [3] 16, 191; Jungfleisch, Ph. [3] 17, 585).

The quinine may also be separated, but less satisfactorily, by extracting the total alkaloid with ether, in which the other alkaloids, especially cinchonine, are much less soluble.

Properties.—Amorphous and anhydrous when precipitated by alkalis from solutions of its salts, but crystallises with $3H_2O$ from a solution in dilute alcohol or aqueous ammonia. Crystalline mono- and di- hydrates have also been described, as well as an amorphous hydrate containing $9H_2O$. These hydrates lose the whole of their water by prolonged exposure over sulphuric acid, or at 100°, and more rapidly at 110–120°. The ordinary trihydrate melts at 57°; the anhydrous alkaloid at 176°; 172·8° (cor.) (Lenz, Fr. 27, 559). Quinine is very slightly soluble in cold water (1 in 1,960 at 15°), but is rather less insoluble in hot water. The solubility in water is increased by the presence of alkalis, especially ammonia, which readily dissolves the alkaloid.

The aqueous solution is bitter and alkaline to litmus. The following quantities of quinine trihydrate are dissolved by 100 parts of the respective solvents at 15°: absolute alcohol, 88·2 parts; chloroform, 51·9 parts; ether, 4·42 parts. Also soluble in carbon disulphide, benzene, amyl alcohol, and petroleum spirit. Quinine is lævorotatory; for the anhydrous alkaloid $[\alpha]_D = -106{\cdot}6°$. For determinations of the rotatory power in alcohol and ether, *v.* Hesse (A. 176, 205).

Quinine readily dissolves in dilute acids, forming salts. The acid solutions of the salts show a magnificent blue fluorescence if the acid used contains oxygen (*e.g.* sulphuric acid), but not if the acid contains no oxygen (*e.g.* hydrochloric acid). In the formation of salts quinine behaves as a diacidic base, unlike most of the vegetable alkaloids, which are monacidic. The salts ordinarily met with, however, contain one mol. prop. of a monobasic acid to one of quinine, or one mol. prop. of a dibasic acid to two of quinine, &c. Nearly all the quinine salts crystallise, and are readily soluble in water and alcohol. The *hydrochloride* $\bar{B}.HCl,2H_2O$, prepared by dissolving the alkaloid in dilute hydrochloric acid, crystallises in long, silky needles, soluble in water, alcohol, and chloroform. Its solutions are lævorotatory. The *di-hydrochloride* $\bar{B}.2HCl$ is produced when dry hydrochloric acid gas combines with quinine. The *normal sulphate* or *di-quinine sulphate* $\bar{B}_2.H_2SO_4,8H_2O$, sometimes called ‘bisulphate,’ is the ordinary commercial sulphate of quinine. It is prepared by exactly neutralising warm dilute sulphuric acid with the alkaloid. When the crystals are exposed to air they effloresce and gradually lose $1H_2O$. The salt as usually met with contains about $7\frac{1}{2}H_2O$. Quinine sulphate is very slightly soluble in water (1 in 740 at 15°), and differs in this respect from the normal sulphates of the other principal cinchona alkaloids, all of which are more soluble. In boiling water quinine sulphate is far more soluble (1 in 30), and may readily be obtained in crystals by cooling the solution. The aqueous solution is very bitter and slightly fluorescent. Alcohol dissolves the sulphate much more easily than water (1 in 65 at 15°; 1 in 3 at b.p.). The salt is slightly soluble in chloroform (1 in 1000), and almost insoluble in ether. Dilute acids dissolve large quantities of quinine sulphate; sulphuric acid converts it into the very soluble *acid sulphate* $\bar{B}_2.(H_2SO_4)_2$ or $B.H_2SO_4$.

Quinine sulphate, like the alkaloid, is lævorotatory. In alcohol, at 15° $[\alpha]_D = -166{\cdot}36°$; for the anhydrous sulphate in water, $[\alpha]_D = -233{\cdot}75°$ (Hesse).

The salt of commerce is liable to be impure from the presence of the sulphates of other cinchona alkaloids. It may be purified by recrystallisation from water, or, better, by dissolving 1 part of the commercial salt in about 30 parts of hot water rendered just acid with sulphuric acid. The crystals which separate are washed with cold water and dried in the air (Hesse, A. 205, 218). For the methods of estimating the amount of pure salt in the commercial sulphate, see later, *Detection and estimation of quinine.*

The *acid sulphate* or *mono-quinine sulphate* $\bar{B}.H_2SO_4,7H_2O$ is produced when the normal sulphate is dissolved in dilute sulphuric acid (Hesse, A. 166, 221; 176, 214). The rhombic crystals effloresce in air and lose their water at 100°. The salt is very soluble in water (1 in 11 at 13°; 1 in 8 at 22°); less soluble in alcohol. The aqueous solution is extremely bitter, and exhibits an intense blue fluorescence, which is quite perceptible in very dilute solutions. The acid sulphates of cinchonine and cinchonidine do not produce this effect, but it is observed with the acid sulphate of quinidine. By dissolving the acid sulphate in sulphuric acid a salt containing an additional proportion of sulphuric acid $B.2H_2SO_4,7H_2O$ may be obtained (Hesse, A. 166, 222).

Quinine and its salts are poisonous to animals, but not to man. In consequence of its marked antipyretic and tonic action, it is a valuable therapeutic agent. A large proportion of the quinine taken internally is excreted unchanged in the urine.

Reactions and constitution.—The most striking qualitative reaction of quinine is that known as the thalleioquin (*θαλλός*, a young twig), colour reaction. It is observed when weak chlorine-water or bromine-water is gradually added to an acidified solution of quinine sulphate until a permanent faint yellow colouration is perceptible; excess of the halogen must be avoided. Ammonia solution is at once added to this liquid, drop by drop, when a dark-green colouration or precipitate makes its appearance. If the green liquid is acidified, its colour changes to red. This reaction, which may be obtained with dilute solutions, is also given by some other alkaloids of this group, notably by quinidine, but cinchonine and cinchonidine do not exhibit it. Ammonia precipitates the alkaloid from solutions of its salts, the precipitate being soluble in excess; quinidine and cinchonidine are less soluble in solution of ammonia; cinchonine almost insoluble. Potash and soda also precipitate salts of quinine, but the alkaloid is only slightly dissolved by excess of these alkalis. The precipitated quinine is readily soluble in ether, quinidine is less soluble, cinchonidine still less soluble, whilst cinchonine is nearly insoluble.

When an alcoholic solution of quinine sulphate, acidified with dilute sulphuric acid, is mixed with an alcoholic solution of iodine, a reddish precipitate is thrown down, which dissolves when the liquid is heated, and on cooling separates in iridescent crystals, which are green by reflected light and red by transmitted light. This substance is an iodosulphate of quinine or periodide of quinine sulphate ($\bar{B}_4.(H_2SO_4)_3(HI)_2I_4,xH_2O$), and has been called 'herapathite,' after its discoverer Herapath. Similar compounds may be formed from the sulphates of other cinchona alkaloids; and, since they are more soluble than the quinine compound, De Vrij has proposed a method of estimating quinine in which the herapathite is collected and weighed, when it will represent 55·055 p.c. of its weight of quinine (De Vrij, Ph. [3] 6, 461).

Moderately concentrated solutions of quinine salts are precipitated by ammonium oxalate, the crystalline quinine oxalate ($\bar{B}_2.H_2C_2O_4,6H_2O$) being sparingly soluble.

Sodium tartrate, or Rochelle salt (potassium sodium tartrate), in aqueous solution precipitates moderately concentrated solutions of quinine salts. The quinine tartrate $\bar{B}_2.H_2C_4H_4O_6,H_2O$ is much less soluble than the quinidine and cinchonine tartrates, but is rather more soluble than cinchonidine tartrate. These facts are utilised in the separation and estimation of quinine and cinchonidine.

Quinine is remarkable in forming a large number of compounds, many of which are crystalline, with different organic bodies, hydrocarbons of the benzene series, phenols, aldehydes, ureas, &c.

In its combinations with alkyl iodides, quinine behaves as a tertiary diamine, *e.g.* combines with one or two molecular proportions of methyl iodide.

By heating a solution of quinine in glycerine to 180–200° it is converted into the amorphous isomeride *quinicine*, which, according to Hesse, is not the same as the amorphous alkaloid quinoïdine contained in cinchona bark. The salts of quinine are also converted into salts of quinicine on prolonged heating, especially in presence of acids.

Quinine furnishes a mono-benzoyl and a mono-acetyl derivative, as well as a mono-chloro- derivative by the action of phosphoric chloride. It therefore contains one hydroxyl group.

When quinine is heated with strong hydrochloric acid, one mol. prop. of methyl chloride is produced, together with a base which has been called *apo-quinine* ($C_{19}H_{22}N_2O_2$); it contains two hydroxyl groups. This reaction proves that quinine contains a methoxyl (OCH_3) group (Hesse, A. 205, 323; Zorn, J. pr. 4, 44; 8, 279).

When brought into contact with a mixture of zinc and dilute sulphuric acid, quinine combines with hydrogen to form the *dihydride* ($C_{20}H_{26}N_2O_2$). Fused with alkali, quinine furnishes chiefly *quinolidine* ($C_{10}H_9NO$), which is para-methoxy-quinoline (Skraup, M. 3, 557; 6, 760). When oxidised with nitric acid or with acid permanganate, quinine, like cinchonine, yields *cinchomeronic acid* (pyridine-dicarboxylic acid $C_5H_3N(COOH)_2$), together with a pyridine-tricarboxylic acid and other substances. By oxidation with chromic acid, quinine furnishes *quininic acid* (methoxy-quinoline carboxylic acid $C_{11}H_9NO_3$), which is the para-methoxyl derivative of a similar acid (cinchoninic acid $C_{10}H_7NO_2$) obtained under the same conditions from cinchonine.

These and other results lead to the conclusion that quinine contains two quinoline residues, and is the para-methoxyl derivative of cinchonine (Skraup, M. 2, 587; 4, 695; B. 12, 1104); *v.* also *Cinchonine.* According to Grimaux and Arnaud, quinine is the methyl derivative of cupreine (C. R. 112, 774, 1364), and may be produced from cupreine by heating it in a sealed tube at 100° with sodium methoxide and methyl chloride; the methyl group takes the place of the hydroxylic hydrogen, producing a methoxyl group.

Detection and estimation.—Quinine may be detected by means of the properties and reactions described above; the fluorescence of solutions of the acid sulphate, the solubility of the alkaloid in ether, and the thalleioquin reaction being especially useful.

For the estimation of quinine in cinchona bark several methods have been suggested. The total alkaloids must first be extracted. This may be accomplished by the following method (Prescott), which is a slight modification of that recommended in the German Pharmacopœia, having been originally proposed by Prollius (Ar. Ph. 219, 85). The solvent employed is made by mixing 85 grms. of ether (sp.gr. ·724–·728) with 10 grms. of alcohol (sp.gr. ·830–·834) and 5 grms. of aqueous ammonia (sp.gr. ·960). Twenty grms. of the cinchona bark, very finely powdered, are mixed in a stoppered bottle with 200 grms. of the solvent. After standing and occasionally agitating for a few hours—or, according to De Vrij, for one hour—any loss of the liquid from evaporation is compensated for by adding the requisite weight of the solvent. About 120 grms. of the clear solution are poured off, and distilled or evaporated to dryness. The weight of this residue is sometimes taken as that of the total alkaloid, but it has been frequently pointed out that it is not entirely composed of alkaloid. To obtain the weight of the pure total alkaloid, the residue should be dissolved in dilute hydrochloric acid, the solution filtered, made alkaline with ammonia, and the alkaloid dissolved out with chloroform in the usual way; or the alkaloid may be precipitated from the acid solution with a very slight excess of aqueous potash, collected, washed, and weighed.

Another slight modification of the process described in the last German Pharmacopœia (1890) has been proposed by Haubensak (C. C. 1891, i. 1006, and C. J. 60, 1402), and is said to afford satisfactory results.

Flückiger (*l.c.*) has proposed to liberate the alkaloids from the bark by mixing with lime and water, instead of ammonia, and to exhaust the dried mixture with boiling ether in an extraction apparatus. Carles (Fr. 9, 497) recommends the liberation of the alkaloids by means of lime and extraction with boiling chloroform. The British Pharmacopœia (1885) also recommends the use of lime, and, as the solvent, a mixture of one volume of amyl alcohol with three of benzene. The United States Pharmacopœia also employs lime for the liberation of the alkaloid, but suggests alcohol for its extraction. Whenever a solvent not soluble in water is employed, the alkaloids may be removed from it by agitation with a dilute acid; or the solvent may be distilled, and the residue dissolved in dilute acid. The total alkaloid is precipitated from the acid solution with a slight excess of an alkali (ammonia), the precipitate being collected and washed, or the liberated alkaloid may be dissolved by agitation with chloroform, which is finally evaporated and the residue weighed. For a criticism of the different methods of estimating the total alkaloids, *v.* Burg (Fr. 4, 273; 9, 305).

The principal methods which have been proposed for the separation and estimation of the quinine in the total alkaloids depend upon the smaller solubility of the quinine sulphate, or the smaller solubility of the quinine (and cinchonidine) tartrate, or the greater solubility of quinine in ether.

The use of ether is not to be recommended for the separation of the quinine, since it has been shown that in presence of each other there is not the same difference between the respective solubilities of quinine, quinidine, and cinchonidine as when they are separately dissolved in ether, and that in consequence of the greater solubility of cinchonidine in the presence of quinine, the results of the estimation of quinine by this method are invariably too high. Nevertheless, the amount of 'ether-soluble alkaloid' is often accepted in commerce as a rough indication of the quantity of quinine in the total alkaloid.

The following method, a slight modification of that given in the United States Pharmacopœia (Prescott), is said to be accurate. A quantity (1–5 grms.) of the total alkaloid is weighed in a beaker, a small quantity of warm water is added, and the mixture titrated with decinormal sulphuric acid until it is just acid to litmus. The solution is heated for about 15 minutes on the water-bath, and at the end of this time should still be feebly acid. The warm liquid is now titrated to exact neutrality with decinormal soda solution. The number of c.c. of soda solution required, deducted from the number of c.c. of acid used, gives the number of c.c. of acid neutralised by the total alkaloid, and this number multiplied by ·03 ought to give a close approximation to the amount in grms. of total alkaloid originally taken.

The amount of total alkaloid having been thus verified by titration, the neutralised liquid is diluted with water until its weight is 70 times that of the total alkaloid, and then heated to about 90° for five minutes. It is now cooled to 15°, and kept at this temperature for half an hour. If crystals have not separated, there is not more than eight p.c. of quinine in the total alkaloid. As a rule crystals will be deposited, and these must be collected on a small weighed filter, and washed with sufficient cold water (15°) to make the total weight of filtrate equal to 90 times that of the total alkaloid present. The crystals are dried at 100°, and weighed as anhydrous sulphate of quinine. To this weight must be added ·12 p.c. of the weight of the filtrate and washings, in order to compensate for the loss of the sulphate through its solubility in water at 15°.

The British Pharmacopœia (1885) recommends the following method by means of which the quinine and cinchonidine are estimated together as tartrates. The total alkaloids (from about twelve grms. of bark) are first obtained and dissolved in diluted hydrochloric acid. The warm liquid is exactly neutralised with ammonia, and evaporated until it has the volume of about 10 c.c. To this liquid is added a solution made by dissolving about one grm. of Rochelle salt in twice its weight of water, and the mixture is well stirred. After having stood for one hour, the precipitated tartrates of quinine and cinchonidine are filtered, washed, dried, and the mixture of anhydrous tartrates weighed. It has been proposed to estimate the amount of quinine present in the mixture of tartrates by a polariscopic method depending on the fact that the specific rotation of cinchonidine tartrate ($[\alpha]_D = -137{\cdot}67°$ for the anhydrous tartrate) is much smaller than that of quinine tartrate

($[\alpha]_D = -220°$ for the anhydrous tartrate) (Koppeschaar, Fr. 24, 362; Oudemans, A. 182, 33).

Estimation of the quinine in the commercial sulphate.—Commercial quinine sulphate is rarely, if ever, quite pure. That intended for medicinal use should not contain 'much more than 5 p.c. of the sulphates of other cinchona alkaloids' (Brit. Pharm. 1885). The principal impurity is usually cinchonidine sulphate, but there may also be present the sulphates of quinidine and cinchonine, whilst if the alkaloid has been derived from cuprea bark the sulphate of cupreine may be found.

The various methods of examining commercial quinine sulphate for the sulphates of other cinchona alkaloids depend either on the greater solubility of the quinine in a definite volume of aqueous ammonia (Kerner's test), or in a definite volume of ether (the so-called 'Liebig's test'), or on a combination of these two facts (Hesse's test).

The German Pharmacopœia (1882) gives the following directions for the application of Kerner's test. Two grms. of the quinine sulphate are agitated with 20 c.c. of water at 15°, and the mixture allowed to stand for 30 minutes; 5 c.c. of the clear solution are placed in a test tube, and aqueous ammonia (rel. dens. ·960) added in small quantities at a time until the precipitated alkaloid is dissolved. Kerner's test is said to be more delicate if the mixture of water and quinine sulphate is first heated on the water-bath for half an hour and then cooled to 15° (Paul, Ph. [3] 7, 653). This modification of the test is introduced into the new German Pharmacopœia (1890), the digestion being effected at from 60–65°, and the mixture then cooled to 15° and kept at that temperature for two hours. Five c.c. of the filtrate are then precipitated with aqueous ammonia, which is gradually added until the precipitate is just re-dissolved. The German Pharmacopœia states that not more than 4 c.c. of aqueous ammonia should be required to form and re-dissolve the precipitate.

The French and United States Pharmacopœias direct that 7 c.c. of aqueous ammonia be added at once to the whole of the filtrate. Any precipitate which remains, or is deposited after some hours, is collected and weighed; this indicates the proportion of foreign alkaloid present. If the ammoniacal liquid remains clear, there cannot be more than one per cent. of cinchonine or quinidine present or more than traces of cinchonidine. Five c.c. of the liquid evaporated to dryness on the water-bath ought not to yield more than ·015 grm. of residue.

Kerner (Ar. Ph. [3] 17, 438) has proposed to apply his method volumetrically by adding the ammonia solution from a finely graduated burette, and observing how much is required to produce a clear solution as compared with that needed for pure quinine sulphate (*cf.* Ruddiman, C. N. 58, 202, 216, 226). The test ascribed to Liebig, apparently erroneously, which depends on the different solubilities of the cinchona alkaloids in ether, is unsatisfactory for the reasons mentioned above.

Hesse (Ar. Ph. [3] 13, 490) has proposed to combine 'Liebig's' and Kerner's test into one process. A slight modification of this method is adopted in the British Pharmacopœia (1885) for the detection of cinchonidine and cinchonine. About 6 grms. of the quinine sulphate are dissolved in about 160 c.c. of boiling water, containing 'three or four drops of diluted sulphuric acid' (13·6 p.c.). The solution when cold is filtered from the quinine sulphate which has crystallised. The clear liquid is placed in a flask, so that the meniscus is situated in the lower portion of the neck. Ether is now added until, after shaking, a distinct layer of ether remains undissolved. Ammonia is then added in slight excess, and the mixture well shaken until the precipitated alkaloid is just re-dissolved. After standing for some hours, any crystals which may have separated are removed, washed with a little ether, dried, and weighed. Four grms. of this alkaloid correspond with 5 grms. of crystallised sulphate of cinchonidine or cinchonine. This method is trustworthy if the addition of 'the three or four drops of diluted sulphuric acid' is omitted (Paul, Ph. [3] 17, 647; 19, 665). For the estimation of cinchonidine sulphate when this alkaloidal salt alone is present in the quinine sulphate, Hesse (A. 205, 217; Ph. [3] 15, 869) has proposed an optical method depending on the fact that the cinchonidine sulphate exerts a much smaller rotation of the polarised ray than an equal weight of quinine sulphate. Much difference of opinion prevails with respect to the accuracy of this method as compared with the chemical processes. On the whole it would appear that one of the chemical methods of separation is to be preferred (*v.* also *Cinchonidine*). Quinidine, if present, would not be separated in the foregoing test, and therefore the British Pharmacopœia includes the following method, which is based on the fact that quinidine sulphate is more soluble in the acidified water than quinine sulphate, and that of the two hydriodides, the quinidine hydriodide is less soluble in water. About three grms. of the quinine sulphate are crystallised from acidulated water as above described. A little alcohol is added to the filtrate (to dissolve the hydriodide of the amorphous alkaloid), together with a strong solution of potassium iodide. The precipitated quinidine hydriodide is collected, washed with a little water, and weighed. Its weight is approximately equivalent to that of the crystallised quinidine sulphate.

The *cupreine sulphate* (*v. Cupreine*) may be found and estimated by taking advantage of the slight solubility of cupreine in ether. The cupreine sulphate, being but sparingly soluble in cold water, will be mixed with the recrystallised quinine sulphate which was removed in testing for cinchonidine and cinchonine. The quinine and cupreine sulphates are mixed with 28 c.c. of ether and 7 c.c. of aqueous ammonia (10 p.c.). After shaking the mixture the ethereal solution is removed and added to that obtained in the test for cinchonidine and cinchonine, out of which these alkaloids had crystallised. The ethereal solutions are now agitated with about 7 c.c. of aqueous soda (10 p.c.), which dissolves the cupreine. The ether is removed, the alkaline solution washed with more ether, and finally heated to 100°.

The hot liquid is exactly neutralised with dilute sulphuric acid, and when the solution is cold the cupreine sulphate which has crystallised out is collected, dried, and weighed.

For further information concerning the detection, separation, and estimation of quinine and the other cinchona alkaloids, *v.* Flückiger, Die Chinarinde; Dragendorff, Plant Analysis; Prescott, Organic Analysis. For a comparison of the various methods of examining commercial quinine sulphate, *v.* Lenz, Fr. 27, 549.

Quinidine or **Conchinine** $C_{20}H_{24}N_2O_2$. This isomeride of quinine is contained in small quantity in most of the ordinary cinchona barks, especially in *China Cuprea* (Remijia) and *Cinchona Calisaya*, which sometimes contain as much as 3 per cent. (Hesse, A. 174, 338). It is most conveniently procured from the amorphous mixture of cinchona alkaloids commercially known as 'quinetum.' The powdered quinoïdine is extracted with ether, and the ethereal solution shaken with dilute sulphuric acid. The neutralised aqueous liquid is precipitated with a strong solution of Rochelle salt, and the concentrated filtrate, decolourised if necessary with charcoal, precipitated with a strong solution of potassium iodide. The impure quinidine hydriodide is washed and dissolved, and the alkaloid precipitated from the solution with ammonia. The precipitated alkaloid is now dissolved in dilute acetic acid, and, if necessary, again decolourised with charcoal. The alkaloid is then reprecipitated with ammonia, and crystallised from boiling alcohol (Hesse, A. 146, 357; 166, 232).

Properties.—Large prismatic crystals containing $2\frac{1}{2}H_2O$, which lose $\frac{1}{2}H_2O$ on exposure to air or on recrystallising from ether, and $1H_2O$ on crystallising from boiling water (Hesse, B. 10, 2154).

The dry alkaloid melts at 171·5° (cor.) (Lenz, Fr. 27, 571). Dextrorotatory (Hesse, A. 174, 337; 182, 139). Very slightly soluble in water (1 in 2,000 at 15°; 1 in 750 at 100°), more soluble in alcohol (1 in 26 at 20°), and in ether (1 in 22 at 20°); also dissolved by amyl alcohol, benzene, and chloroform, but not appreciably by light petroleum. Dilute acids dissolve the alkaloid abundantly, and, like quinine, the solutions, if acid with sulphuric acid or other oxygenated acid, exhibit a blue fluorescence. Like quinine, quinidine is a diacidic base, but only its normal salts are usually met with. The *normal sulphate* $\bar{B}_2.H_2SO_4,2H_2O$ is more soluble in cold water than the quinine salt (1 in 100 at 15°), and also in chloroform (1 in 20 at 15°). The *acid sulphate* $\bar{B}.H_2SO_4$ is very soluble in water, and its solution is highly fluorescent. The *hydriodide* $\bar{B}.HI$ is an important salt, since it is much less soluble in water (1 in 1250 at 15°) than the hydriodides of the other cinchona alkaloids, and is therefore employed in isolating and in estimating quinidine. It is precipitated at once, or from dilute solutions after standing and stirring, as a crystalline powder when potassium iodide is added to a neutral or slightly acid solution of a quinidine salt. In presence of much acid the soluble *dihydriodide* $\bar{B}.(HI)_2$ is produced.

Quinidine and its salts have a very bitter taste, and exert a physiological and therapeutic action very like that of quinine. For a list of the principal salts *v.* CINCHONA BASES in WATTS' DICTIONARY OF CHEMISTRY, by Muir a. Morley.

Reactions.—The chief reactions of quinidine resemble those of quinine. It affords the thalleioquin colour reaction (*v. Quinine*). Its derivatives and decomposition products are in most cases almost or quite identical with those of quinine, from which it would seem to differ only in the position which the hydroxyl group occupies in the molecule.

Detection and estimation.—Quinidine may be detected by the fluorescence of acid solutions of its salts, by its affording the thalleioquin reaction, by solutions of its salts not being precipitated by solution of Rochelle salt (distinction from quinine and cinchonidine), and by the formation of the insoluble hydriodide &c., and by other properties described above. For the estimation of the alkaloid in cinchona bark, advantage may be taken of the solubility of the normal sulphate in chloroform or cold water, the solubility of quinidine tartrate, and the formation of the hydriodide, which is collected and weighed. The quinine and cinchonidine having been removed from the total alkaloids as tartrates (*v. Estimation of quinine*), the filtrate, somewhat concentrated, is precipitated with a saturated solution of potassium iodide. After standing for an hour the quinidine hydriodide is collected, washed with a little cold water, dried, and weighed.

For the estimation of quinidine in commercial sulphate of quinine *v. Quinine sulphate.*

Cinchonine $C_{19}H_{22}N_2O$ is an alkaloid commonly occurring in cinchona bark to the extent of about ·2–2 p.c. It may be readily prepared from the mother-liquor remaining from the preparation of quinine (*q. v.*). This solution, which contains cinchonine sulphate, is precipitated with soda, and the precipitate crystallised from its solution in alcohol. The alkaloid thus obtained is purified by converting it into the normal sulphate, which is repeatedly crystallised from water (Hesse, A. 122, 226); or the precipitate produced by the soda may be dried and digested with cold ether in which cinchonine is very slightly soluble. The residue is crystallised from alcohol.

Properties.—Anhydrous monoclinic prisms (from alcohol), or amorphous when precipitated; m.p. 255·4° (cor.) (Lenz, Fr. 27, 572), 248–252° (Hesse, A. 205, 211). At a higher temperature it sublimes, with some decomposition. Almost insoluble in water (1 in 3,670 at 20°), slightly soluble in ether (rel. dens. ·730, 1 in 371 at 10°) and in benzene, more soluble in alcohol (rel. dens. ·852, 1 in 126 at 20°) and in chloroform (1 in 356 at 17°), but most readily in a mixture of chloroform and alcohol, which dissolves more than either liquid alone. Soluble in amyl alcohol, nearly insoluble in aqueous ammonia, in light petroleum, and in absolute alcohol. Readily soluble in dilute acids, but the solutions are not fluorescent. Dextrorotatory, at 17° $[\alpha]_D = +223{\cdot}3°$ (Oudemans, A. 182, 44).

Cinchonine is a diacidic base, but the ordinary salts are normal. In composition they correspond with those of quinine. The *normal sulphate* $B_2.H_2SO_4,2H_2O$ is soluble in water (1 in 70 at 15°; 1 in 14 at 100°); soluble also in alcohol (1 in 6 at 15°), and in chloroform (1 in

60 at 15°). The acid sulphate $B.H_2SO_4,4H_2O$ is very soluble in water, but, unlike the corresponding quinine and quinidine salts, its aqueous solutions are not fluorescent, although commercial specimens of the sulphate, when dissolved in dilute sulphuric acid, are usually slightly fluorescent owing to the presence of quinine or quinidine. The salts of cinchonine are very bitter, and appear to exert the same physiological and therapeutic action as quinine, although much less powerfully. For a list of the principal salts *v.* CINCHONINE in WATTS' DICTIONARY OF CHEMISTRY.

Like quinine, cinchonine combines with phenols and certain other organic compounds.

Reactions.—The reactions of cinchonine are similar to those of quinine. It does not, however, afford the thalleioquin colour reaction.

In its combinations with methyl iodide cinchonine, like quinine, acts as a tertiary diamine.

When heated with glycerine to 180–210°, it is changed into its amorphous isomeride *cinchonicine*, which is also formed when the sulphate is heated. Like quinine, cinchonine forms a dihydride ($C_{19}H_{24}N_2O$). It also resembles quinine in furnishing mono-benzoyl and mono-acetyl derivatives, and therefore, like it, contains a single hydroxyl group.

When strongly heated with hydrochloric acid, cinchonine does not furnish methyl chloride. It therefore does not contain methoxyl. When oxidised with chromic acid, cinchonine affords chiefly *cinchoninic acid* (γ-quinoline-carboxylic acid) (Königs, B. 12, 97; Skraup, A. 201, 294).

By the action of nitric acid there are produced, besides *cinchoninic acid*, *cinchomeronic acid* (pyridine-dicarboxylic acid) and other substances (Weidel, A. 173, 76). By distillation over zinc-dust, cinchonine yields quinoline and pyridine derivatives.

When distilled with alkali, a large quantity of quinoline and methyl-pyridines are produced, together with several acids of the acetic series. Phosphoric chloride replaces the hydroxyl group in cinchonine by chlorine, and this chloro-cinchonine ($C_{19}H_{21}ClN_2$) when heated with potash loses hydrochloric acid yielding *cinchene* ($C_{19}H_{20}N_2$), which is a tertiary base furnishing cinchoninic acid on oxidation. When strongly heated with hydriodic acid, cinchene affords *apo-cinchene* $C_{19}H_{19}NO$ and ammonia. Apocinchene contains hydroxyl, and acts like a phenol, from which it may be inferred that the hydroxyl group in this compound is probably attached to a benzene nucleus. The reactions of cinchonine point to the conclusion that it is a di-quinoline derivative, but its exact constitution is still a matter of doubt.

Detection and estimation.—Cinchonine is readily distinguished from quinine and quinidine by not giving the thalleioquin reaction, as well as by other properties described above. From cinchonidine, which it resembles in not giving the colour reaction, it may be distinguished by its slight solubility in aqueous ammonia and in ether, and also by the solubility of its normal sulphate in chloroform. The amount of cinchonine contained in the total alkaloids of cinchona bark may be estimated in the filtrate and washings from which the quinidine has been separated as hydriodide (*v. Quinidine*), by precipitating it with soda, and digesting the dried precipitate with a small quantity of ether in order to dissolve the amorphous alkaloid. The residue is dried and weighed as cinchonine.

For the detection and estimation of cinchonine in commercial sulphate of quinine *v. Quinine sulphate.*

Cinchonidine $C_{19}H_{22}N_2O$, an isomeride of cinchonine, found in most varieties of cinchona bark to the extent of from ·5 – 5 p.c. Cinchonidine sulphate has been largely used in medicine as a substitute for quinine.

Preparation.—The total alkaloids having been extracted from the cinchona bark (*v. Quinine*), and the crystallised quinine sulphate separated, the aqueous solution (containing cinchonidine, cinchonine, and quinidine sulphates) is precipitated with ammonia in slight excess, and the precipitate repeatedly extracted with cold ether. The ethereal solution (containing cinchonidine and quinidine) is shaken with dilute hydrochloric acid, when the alkaloidal hydrochlorides pass into the aqueous liquid, which is neutralised, and the cinchonidine precipitated as tartrate by the addition of solution of Rochelle salt. The precipitate is dissolved in hydrochloric acid, and precipitated with ammonia in slight excess. The alkaloid thus obtained is crystallised from its solution in boiling alcohol, then converted into the normal sulphate, which is crystallised. The crystallised salt is dissolved in 25 parts of boiling water, and the solution cooled to 35°, when any crystals which may have separated are removed and twice recrystallised. By precipitating a solution of this salt with ammonia and crystallising the precipitate from alcohol, pure cinchonidine is obtained (Hesse, A. 135, 333; 205, 196).

The commercial sulphate of cinchonidine may be purified by this process. It generally contains small quantities of the sulphates of other cinchona alkaloids, especially *homo-cinchonidine*, an isomeride of cinchonidine which occurs with it in cinchona barks (Hesse, A. 205, 203).

Properties.—Anhydrous prismatic crystals, which melt at 207·2° (cor.) (Lenz, Fr. 27, 564); 200–201° (Hesse, B. 14, 1888). Slightly soluble in water (1 in 1,680 at 10°). Soluble in alcohol (1 in 16·3 at 13°), and in ether (1 in 188 at 15°). Readily soluble in chloroform and amyl alcohol. Slightly soluble in aqueous ammonia. Very soluble in dilute acids. Lævorotatory, $[\alpha]_D = -107{\cdot}48°$ in alcohol (Hesse, A. 176, 219; 181, 137).

Cinchonidine is a diacidic base, but the salts usually met with are normal. The *normal sulphate* $B_2.H_2SO_4,6H_2O$ is used in medicine. It is readily soluble in hot water, but only sparingly in cold (1 in 97·5 at 12°; 1 in 67 at 22°). The *acid sulphate* $B.H_2SO_4,5H_2O$ is very soluble in water. Its solutions are not fluorescent.

Cinchonidine and its salts are very bitter. Their therapeutic action is similar to, but weaker than, that of quinine. The administration of large doses is said to be attended with danger.

For a list of the principal salts of cinchonidine *v.* CINCHONIDINE in WATTS' DICTIONARY OF CHEMISTRY, by Muir a. Morley.

Reactions.—The principal reactions of cinchonidine resemble those of its isomeride cinchonine. By the action of phosphoric chloride the *chloro- derivative* $C_{19}H_{21}ClN_2$, isomeric with the corresponding cinchonine derivative, is obtained. Like cinchonine, therefore, cinchonidine contains a single hydroxyl group. Although this chloro-cinchonidine is isomeric, and not identical with chloro-cinchonine, when acted on by potash it furnishes the same cinchene (*v. Cinchonine*).

The products of the oxidation of cinchonidine by nitric acid and chromic acid are similar to those afforded by cinchonine. When fused with potash, cinchonidine furnishes *quinoline*. The differences between cinchonidine and cinchonine are apparently dependent for the most part on the different positions occupied by the hydroxyl group.

Detection and estimation.—Cinchonidine is readily distinguished from quinine and quinidine by not affording the thalleioquin reaction, and in its acid salts not being fluorescent. It differs from cinchonine in its greater solubility in ether, as well as by the slight solubility of its tartrate &c. It may be identified by the properties described above. Cinchonidine may be estimated in the total alkaloids from cinchona bark by precipitating the liquid from which the quinine has been removed by crystallisation as sulphate with a strong solution of Rochelle salt, when the cinchonidine tartrate is precipitated. After standing some time, the precipitate is collected, dried, and the anhydrous tartrate weighed.

Another method consists in determining the amount of quinine in a portion of the total alkaloids, by crystallisation as sulphate, and in a second portion of the total alkaloids precipitating the quinine and the cinchonidine as tartrates (*v. Estimation of quinine*). The amount of quinine sulphate already found is then calculated into tartrate, and this quantity is deducted from the weight of the mixed tartrates; the remainder is the amount of cinchonidine tartrate.

It has also been proposed to separate quinine and cinchonidine (liberated from the tartrates) by dissolving out the quinine with ether, but the method does not afford accurate results, since the solubility of cinchonidine in ether is increased by the presence of quinine, owing apparently to the formation of a compound of the two alkaloids.

A polariscopic method of estimating cinchonidine salts in presence of quinine salts has been suggested, there being a considerable difference in the rotatory power of cinchonidine and quinine compounds (*v. Estimation of quinine*). The method would seem to be trustworthy, especially for the estimation of cinchonidine sulphate in commercial sulphate of quinine, although some observers have not obtained satisfactory results with it (Hesse, A. 205, 217; Ph. [3] 15, 869; [3] 16, 818; Schäfer, Fr. 26, 655; Koppeschaar, *ibid.* 24, 362; Davies, Ph. [3] 16, 358; Paul, *ibid.* [3] 16, 361).

For other information respecting the estimation of cinchonidine in commercial sulphate of quinine *v. Quinine sulphate.*

Quinamine $C_{19}H_{24}N_2O_2$. An alkaloid found by Hesse in *C. succirubra*, and apparently existing in small quantity in many of the ordinary varieties of cinchona bark (Hesse, A. 166, 266; B. 10, 2157).

Preparation.—The total alkaloids are dissolved in dilute sulphuric acid, and the solution neutralised with ammonia. The quinine and cinchonidine are removed by precipitating the liquid with a strong solution of Rochelle salt, and the filtrate is then precipitated with soda. The washed precipitate is extracted with ether, which dissolves the quinamine. The alkaloid thus obtained is purified by extracting it with dry ether, and crystallising the ethereal residue from alcohol. The alkaloid is finally purified by conversion into the nitrate, which is re-crystallised from water, and the alkaloid regenerated from the pure salt (Hesse, *l.c.*; Oudemans, A. 197, 50).

Properties.—Long silky anhydrous needles; m.p. 172°. Slightly soluble in cold water; very soluble in boiling alcohol, ether, benzene, and light petroleum. Dextrorotatory. Quinamine is coloured yellow by warm sulphuric acid, and orange by nitric acid. The salts are crystalline, and soluble in water.

Conquinamine $C_{19}H_{24}N_2O_2$ is an isomeride of quinidine, with which it occurs in several species of cinchona bark, especially in *C. succirubra* (Hesse, A. 209, 62; Oudemans, A. 209, 38).

Properties.—Crystals; m.p. 121°. Very slightly soluble in water. Soluble in alcohol, chloroform, and ether; dextrorotatory. The salts are crystalline, and soluble in water.

Cupreine $C_{19}H_{22}N_2O_2$ is an alkaloid contained, together with quinine &c., in the bark of *China Cuprea* (*Remijia pedunculata*), a plant closely related to, though distinct from, the cinchonas (Paul a. Cownley, Ph. [3] 15, 221, 401; Hesse, A. 230, 57).

Preparation.—The total alkaloids of cuprea bark are dissolved in dilute sulphuric acid, the solution is exactly neutralised, when the sulphates of cupreine and quinine crystallise out. These salts are dissolved in dilute sulphuric acid, and precipitated with excess of soda, which dissolves the cupreine and some of the quinine. On shaking the mixture with ether, the quinine is dissolved by it, whilst the alkaline solution contains the cupreine. The aqueous liquid is now neutralised with dilute sulphuric acid, when the cupreine sulphate crystallises out. The base is obtained by precipitating a solution of the recrystallised sulphate with ammonia. The precipitated alkaloid is crystallised from its solution in boiling ether and dried. It is then washed with chloroform, and finally crystallised from alcohol (Hesse, *l.c.*).

Properties.—Prisms with $2H_2O$, which lose their water at 120°, and melt at 198°. Slightly soluble in ether and chloroform, more soluble in alcohol. Soluble in aqueous soda and potash; less soluble in aqueous ammonia; lævorotatory. Ferric chloride produces a dark-green colour, and ammonia, after the addition of chlorine water, produces the green colouration known as the thalleioquin reaction (*v. Quinine*).

Cupreine possesses both acid and basic properties. As a base it is diacidic. The normal salts are yellow crystalline solids; the acid salts are colourless, and their solutions are not fluorescent. The acid properties of cupreine resemble those of a phenol. It dissolves in aqueous alkalis, and unites with bases to form definite compounds. One of these is of especial interest, viz. that produced by the combination of cupreine with quinine, which may be effected by dissolving equimolecular proportions of quinine and cupreine in dilute sulphuric acid, precipitating with ammonia, and crystallising from ether. This compound

$$(C_{19}H_{22}N_2O_2.C_{20}H_{22}N_2O_2,4H_2O)$$

was first obtained from the total alkaloids of cuprea bark, and was thought to be a single alkaloid 'homoquinine.' The substance melts at 177°, is lævorotatory, and dissolves with difficulty in ether but readily in alcohol. It behaves as a single diacidic base, and forms well-crystallised salts; the normal sulphate is fluorescent in acid solution. The compound may be resolved into its constituents by precipitating the sulphate with excess of soda, and extracting with ether, which dissolves some of the quinine. By repeating the process a number of times, the two alkaloids may be more or less completely separated (Howard a. Hodgkin, C. J. 41, 66; Hesse, A. 225, 98; 226, 242; 230, 72; Paul a. Cownley, *l.c.*).

For the methods of detecting cupreine in commercial quinine sulphate *v. Quinine.*

Rubijervine *v. Veratrine and the veratrum alkaloids.*

Sabadilline *v. Veratrine and the veratrum alkaloids.*

Sabadine *v. Veratrine and the veratrum alkaloids.*

Sabadinine *v. Veratrine and the veratrum alkaloids.*

Sanguinarine $C_{20}H_{15}NO_4$ occurs in *Sanguinaria canadensis*; m.p. 211°. It is a monacidic base, whose salts form red crystals (König, C. C. 1891, i. 321).

Sarcine *v. Theobromine and the alkaloids of tea and coffee.*

Sinapine $C_{16}H_{23}NO_5$, an alkaloid existing as thiocyanate in white mustard seed, and also produced by the hydrolysis of sinalbine, the glucoside of white mustard (Babo a. Hirsthbrunn, A. 84, 10; Will a. Laubenheimer, A. 199, 162). The base itself is unstable. It is hydrolysed by boiling aqueous alkalis into *choline* and *sinapic acid*

$$C_{16}H_{23}NO_5 + 2H_2O = C_5H_{15}NO_2 + C_{11}H_{12}O_5.$$

Solanine $C_{42}H_{75}NO_{15}$? a substance at once an alkaloid and a glucoside, which occurs in various species of *Solanum* (*S. Dulcamara*, *S. nigrum*) and also in young potato shoots (Desfosses, J. Ph. 6, 374; 7, 414; Zwenger a. Kind, A. 109, 244; 118, 130; 123, 341; Hilger, A. 195, 317; Firbas, M. 10, 541). Much uncertainty still exists with reference to the correct formula for this alkaloid, several different formulæ having been suggested.

Properties.—Prismatic crystals; m.p. 235°. A feeble base, whose salts are decomposed by water. It is an energetic reducing agent, and a powerful poison. When boiled with dilute sulphuric acid it furnishes a sugar (apparently not dextrose) and a base *solanidine* ($C_{26}H_{41}NO_2$?).

Sophorine *v. Cytisine.*

Sparteine $C_{15}H_{26}N_2$, a liquid alkaloid obtained from broom (*Cytisus scoparius* or *Spartium scoparium*) (Stenhouse, A. 78, 15; Mills, A. 125, 71). *V.* also Broom tops.

Properties.—A liquid, heavier than water, b.p. 311° (at 723 mm. in a stream of hydrogen). Slightly soluble in water, soluble in alcohol, ether, and chloroform; insoluble in light petroleum and benzene. The aqueous solution is alkaline, and very bitter. Distils with steam. Lævorotatory, $[\alpha]_D = -146°$ in alcohol (Bamberger, A. 235, 368). Sparteine is a diacidic base, which forms difficultly crystallisable salts. The alkaloid and its salts exert a strong narcotic action.

Reaction.—Sparteine behaves towards alkyl iodides as a tertiary diamine.

It combines with nascent hydrogen, forming *hydrosparteine* $C_{15}H_{28}N_2$. When heated with hydriodic acid, it furnishes a molecular proportion of *methyl iodide.* When oxidised with permanganate, it yields chiefly *formic* and *oxalic* acids (Bamberger, A. 235, 368; Ahrens, B. 20, 2219). When the vapour of sparteine is passed through a red-hot tube, the chief products are *pyridine*, *γ-picoline*, *ethylene*, and *ammonia* (Ahrens, B. 21, 828; 24, 1095). Sparteine evidently contains two pyridine nuclei, and is allied to nicotine, but its exact constitution is not yet established.

Strychnine and the strychnos alkaloids (*v.* also Nux vomica).

Strychnine $C_{21}H_{22}N_2O_4$ the principal alkaloid of *Strychnos Nux-vomica*, *S. Ignatii*, *S. Colubrina*, *S. Ticuté*, and other plants belonging to the natural order *Loganiaceæ.* The nearly allied alkaloid brucine usually occurs with strychnine in these plants. Strychnine was discovered by Pelletier and Caventou in 1817. The existence in *S. Nux-vomica* of the alkaloid *igasurine* described by Desnoix in 1853 is doubtful, later observers having failed to find it. The seeds of *S. Nux-vomica* vary in the amount of total alkaloid (strychnine and brucine) they contain. As little as 1 p.c. has been found, and as much as 5 p.c., in the seeds of the Ceylon nux vomica (Dunstan a. Short, Ph. [3] 15, 1). About one-third of the total alkaloid is strychnine and two-thirds brucine (Dunstan a. Short, Ph. [3] 12, 1053, 15, 1). The seeds of *S. Ignatii* are richer in strychnine than those of *S. Nux-vomica.*

Preparation.—The following process may be used for the extraction of strychnine and brucine from the seeds of *S. Nux-vomica* or *S. Ignatii* (*v.* also Nux vomica). The finely powdered seeds are made into a paste with water and one-fourth of their weight of slaked lime. The mixture is thoroughly dried on the water-bath, and the dry mass finely powdered. The alkaloids are now dissolved from it by hot percolation with a suitable solvent (amyl alcohol, benzene, or chloroform) in an extraction apparatus. The solvent is shaken with dilute sulphuric acid, which removes the alkaloids as sulphates. These salts may be crystallised from the neutral solution, or the alkaloids may be regenerated, and the mixture (strychnine and brucine) extracted with dilute (25 p.c.) alcohol, which dissolves the brucine, and leaves nearly the whole of the strychnine undissolved. It is purified by recrystallisation from alcohol.

Properties.—Rhombic crystals; m.p. 260° (Stoehr, J. pr. [2] 42, 399); 284° (Claus, B. 14, 773); 285° (Beckürts, B. 18, 1235); 268° (Loebisch a. Schoop, M. 6, 858). At higher temperatures some of the alkaloid sublimes unchanged. According to Loebisch (*l.c.*), the alkaloid distils without decomposition at 270° under the reduced pressure of 5 mm. Lævorotatory; in alcoholic solution, $[\alpha]_D = -132{\cdot}07°$ (Bouchardat, A. Ch. [3] 9, 228). Very slightly soluble in water (1 in 6,667, at 15°; 1 in 2,500 at 100°). The aqueous solution, even when largely diluted, has a persistent bitter taste; the bitterness is said to be perceptible in a solution containing 1 part of strychnine in 600,000 parts of water. The alkaloid is insoluble in absolute alcohol and ether, but is dissolved by chloroform, benzene, amyl alcohol, and 90 p.c. alcohol.

Strychnine is a violent poison, giving rise to tetanic spasms, owing to the greatly increased excitability of the spinal cord. Half a grain of the alkaloid has proved fatal to man.

Strychnine is a monacidic base; its salts are, as a rule, crystalline and soluble in water.

Reactions.—Strychnine, which is one of the most stable of the alkaloids, is not coloured by nitric acid or by sulphuric acid. It may be heated to 100° with sulphuric acid without being appreciably affected. When brought into contact with certain oxidising agents, it exhibits a striking colour reaction, which is generally relied on for its detection. If the alkaloid is dissolved in a drop of strong sulphuric acid, and a small piece of potassium bichromate, manganese dioxide, ceric oxide, or potassium permanganate is stirred into the mixture, a magnificent play of colours is observed, beginning with blue, which gradually passes through violet and red to yellow (Marchand, J. Ph. [3] 4, 200). The only other alkaloids which behave exactly like strychnine in this respect are curarine and gelsemine. Several alkaloids, however, give a somewhat similar colour reaction, but most of these are coloured by sulphuric acid alone, and may thus be readily distinguished from strychnine. The presence of foreign organic compounds frequently obscures the colour, and the alkaloid to be tested must, therefore, first be isolated in a nearly pure state, and separated as far as possible from any other alkaloid that may be present. This colour reaction cannot be obtained in the presence of much brucine, the alkaloid which accompanies strychnine in the plant, since it gives a deep-red colouration when oxidised which obscures the play of colours produced by the strychnine. This alkaloid may, however, be removed by oxidation with dilute nitric acid, the strychnine being recovered from the acid liquid by adding ammonia and extracting with chloroform (Shenstone, Ph. [3] 8, 445; Hanriot, C. R. 97, 267), or the mixed alkaloids may be washed with chlorine water, when the brucine is converted into the soluble dichlorobrucine, which dissolves, leaving a residue of strychnine (Beckürts, Ar. Ph. 228, 326). In toxicology, where traces of impurity in the alkaloidal residue would give rise to darkening when the sulphuric acid is added, the residue may be moistened with the strong acid and heated on the water-bath until the impurity is completely decomposed; water is then added, and the strychnine recovered by adding ammonia and extracting with chloroform. A large number of derivatives of strychnine have been prepared, of which only a few call for notice here.

The so-called *hydrate* or *strychnol*

$$C_{21}H_{22}N_2O_2,H_2O$$

is formed when strychnine is heated with sodium ethylate. It is a very stable body, which does not give the characteristic colour reaction of strychnine. Tafel (A. 264, 33; 268, 229) has recently shown that this compound is an imido-acid

$$(C_{20}H_{22}NO(COOH)NH,4H_2O),$$

and he has therefore called it *strychnic acid*, although Plugge (Ar. Ph. [3] 21, 641) has already given this name to an oxidation product $C_{11}H_{11}NO_3$. It is converted into strychnine on being heated to 190° in a stream of hydrogen.

Two other 'hydrates' are also known, which seem to be analogous to strychnic acid, *dihydro-strychnine* $C_{21}H_{22}N_2O_2,2H_2O$ and *trihydro-strychnine* $C_{21}H_{22}N_2O_2,3H_2O$. They are obtained by heating strychnine with baryta water (Gal a. Etard, Bl. [2] 31, 98). The first of these compounds has been shown by Tafel to lose $1H_2O$ at 135°, yielding an imido-acid, which he has called *iso-strychnic acid*. The recent results obtained by this chemist point to the conclusion that strychnine ($C_{20}H_{22}NO.N.CO$) is the anhydride of strychnic acid ($C_{20}H_{22}NO.NH.COOH$). By the action of nitric acid strychnine yields, besides nitro-derivatives, *trinitrophenol* (picric acid), the formation of which indicates the existence of a benzene nucleus in its molecule (Shenstone, C. J. 47, 139). When the alkaloid is distilled with alkali, *indole* and *methyl-indole* (skatole) are formed, together with β-picoline and other bases (Goldschmidt, B. 15, 1977; Stoehr, B. 20, 810, 1108, 2727; J. pr. [2] 42, 399).

It has already been remarked that strychnine acts as a powerful stimulant on the spinal cord. Crum Brown and Fraser have shown that the addition of methyl iodide to strychnine abolishes this characteristic physiological action, the salts of the 'ammonium base' (methyl strychnium) being without action on the spinal cord.

Detection and estimation of strychnine.—Strychnine is readily detected by the properties and reactions described above.

For the estimation of strychnine in nux vomica, Ignatius beans, &c., and in the medicinal preparations made from these plants, the following processes have been devised.

For the seeds of *S. Nux-vomica* or *Ignatii* five grms. of the seeds dried at 100°, and finely ground, are exhausted of alkaloidal salts by hot re-percolation in an extraction apparatus (*v.* EXTRACTION APPARATUS) with chloroform, to which has been added 25 p.c. by volume of alcohol. The solvent rapidly and completely dissolves the whole of the alkaloidal salts. The solution is mixed with about half its volume of dilute sulphuric acid (5 p.c.), and well shaken. The mixture separates into two layers, the alkaloids being in the upper aqueous layer and the colouring matter &c. in the lower layer of chloroform. When the alkaloidal salts have been completely removed from the chloroform by a repetition of this process, the solution of the acid sulphates of strychnine and brucine is made alkaline with ammonia, and extracted with chloroform until the alkaloids are removed. The alkaloidal residue left by the evaporation of the chloroform is dried at 100° and weighed (Dunstan a. Short, Ph. [3] 13, 665, 1053).

For the tincture of nux vomica 50 c.c. of the tincture are evaporated almost to dryness on the water-bath. The residue is dissolved in dilute sulphuric acid, and to the clear acid liquid ammonia is added in excess, and the alkaloid removed by shaking wth chloroform. The residue of alkaloid left by the evaporation of the chloroform is dried at 100° and weighed (Dunstan a. Short, Ph. [3] 14, 292). Tincture of nux vomica is now required by the British Pharmacopœia to contain ·205 p.c. by volume of total alkaloid as estimated by the process above described.

For the extract of nux vomica, about one grm. of the extract is dissolved in about 50 c.c. of 5 p.c. aqueous sodium carbonate, and the liquid twice extracted with half its volume of chloroform. The solution of the alkaloid in chloroform is shaken with half its volume of dilute sulphuric acid, and the chloroform, which contains fat and resin, removed. The clear acid liquid is made alkaline with ammonia, and the alkaloid extracted with chloroform. The solution of the alkaloids in chloroform is evaporated and dried at 100°, and weighed (Dunstan a. Short, Ph. [3] 14, 621). The British Pharmacopœia requires that extract of nux vomica shall yield 15 p.c. of strychine and brucine when analysed as above described.

The alkaloid obtained by all these processes is a mixture of strychnine and brucine. The two alkaloids possess very similar properties, and are not easy to separate. On the large scale an approximate separation may be effected by extracting the residue with dilute alcohol (25 p.c. by volume), which readily dissolves the brucine but only traces of the strychnine.

For quantitative purposes advantage may be taken of the great difference in the solubilities of the ferrocyanides of strychnine and brucine; the strychnine salt, being very slightly soluble in water, separates from dilute acidified solutions as a characteristic granular precipitate, whilst the brucine ferrocyanide, being readily soluble in water, does not separate except from concentrated solutions. When both alkaloids are present, the separation is not quite so sharp as might be anticipated, but it has been proved that sufficiently accurate results for ordinary analytical purposes may be obtained if the following directions are adhered to (Dunstan a. Short, Ph. [3] 14, 621). Any quantity less than 0·2 grm. of the mixed alkaloids is dissolved in about 10 c.c. of dilute sulphuric acid (5 p.c. by volume). The solution is diluted with water to about 175 c.c., and finally made up to 200 c.c. with 5 p.c. aqueous potassium ferrocyanide. The liquid is stirred occasionally, and allowed to stand for about six hours, by which time the strychnine ferrocyanide will have separated as a white granular precipitate. The precipitate is collected, and washed with water just acidulated with sulphuric acid until the washings are scarcely bitter. Since strychnine ferrocyanide is difficult to dry without decomposition, the moist salt is decomposed by the addition of strong ammonia, in which it is completely soluble. The alkaline liquid is twice extracted with chloroform, which removes the strychnine. The solution in chloroform is evaporated in the water-bath to a small volume, the remainder of the chloroform spontaneously evaporated, and the residue finally dried in a covered dish (to avoid loss by spurting) and weighed. The brucine may be estimated by difference, or it may be dissolved from the filtrate and washings made alkaline with ammonia by shaking with chloroform, separating, evaporating, and weighing in the usual manner.

Holtz and Beckürts (Ar. Ph. [3] 25, 313) have proposed to apply this method volumetrically.

A method of separation depending on the greater solubility of brucine picrate has also been proposed (Gerock, Ar. Ph. [3] 27, 158).

Brucine $C_{23}H_{26}N_2O_4$. This alkaloid occurs with strychnine in *S. Nux-vomica* and in other species of *Strychnos*. There is no well-authenticated evidence that brucine is found without strychnine, unless, indeed, we except that of *S. ligustrina* (Bedara, Laut) (Greenish, Ph. [3] 9, 1013). In the seeds of *S. Nux-vomica* about two-thirds of the total alkaloid is brucine (Dunstan a. Short, Ph. [3] 15, 1). In the seeds of *S. Ignatii* the proportion of brucine appears to be smaller.

Preparation.—The total alkaloid having been extracted from the plant by the method described for strychnine, the mixture is repeatedly washed with dilute alcohol (25 p.c. by volume), and the brucine crystallised from the solution, and recrystallised several times from the same solvent or from water, the fractions which crystallise latest being almost, if not quite, pure brucine.

According to Flückiger (Pharm. Chem.), if the mixture of the two alkaloids is converted into the acetates, and the solution is evaporated to dryness on the water-bath, the strychnine acetate undergoes dissociation into the alkaloid and acetic acid, which volatilises. The brucine acetate remains unchanged, and may be dissolved from the residue by cold water and crystallised. For another method which is said to furnish quite pure brucine *v.* Shenstone, C. J. 39, 453, and also NUX VOMICA.

Properties.—Brucine separates from its solutions in water or aqueous alcohol in monoclinic prisms containing $4H_2O$; m.p. 105°. The crystals lose their water at 100°, or on standing over sulphuric acid. The anhydrous substance melts at 178° (Claus, B. 14, 773); lævorotatory, $[\alpha]_D$ in alcohol $= -85°$. Slightly soluble in cold water (1 in 320), twice as soluble in boiling water, very soluble in alcohol, chloroform, and amyl alcohol; insoluble in ether. Brucine and its salts are bitter, and when subcutaneously injected in animals produce a physiological action resembling in kind that of strychnine, but much feebler. When administered internally to animals it produces little or no effect, owing chiefly to the rapidity with which it is eliminated (Brunton, C. J. 47, 143).

Brucine is a monacidic base; the ordinary salts are crystalline, and readily dissolve in water.

Reactions.—Brucine is readily distinguished from strychnine since it does not give rise to the characteristic play of colours when oxidised with chromic acid &c., only an intense red colouration being produced, whilst brucine is further differentiated from strychnine by giving a deep-red colouration when mixed with nitric acid; this is a very delicate test for brucine, and conversely for nitric acid. This red colouration of brucine is distinguished from that produced when some other alkaloids (*e.g.* morphine) are mixed with nitric acid, by the action of stannous chloride or certain other reducing agents, which when cautiously added change the red colouration to violet.

When brucine is oxidised with sulphuric acid and manganese dioxide, methyl alcohol is one of the products (Baumert, A. 70, 337).

Nitric acid furnishes *cacotheline* ($C_{21}H_{22}N_4O_9$), *oxalic acid*, and *methyl nitrite* (Strecker, A. 91, 76; Hanssen, B. 20, 451). When heated with strong hydrochloric acid, brucine evolves rather less than two molecular proportions of *methyl chloride* (Shenstone, C. J. 43, 101; Hanssen, B. 17, 2266). Distilled with potash, brucine affords ammonia, a mixture of *lutidines* and *collidines*, together with *tetrahydride* of *quinoline* (De Coninck, A. Ch. [5] 27, 507; Bl. [2] 42, 100). When lime is used, *β-picoline* identical with that obtained from strychnine is produced (Berend a. Stoehr, J. pr. [2] 42, 415).

The production of *methyl alcohol*, *methyl nitrite*, and of *methyl chloride* from brucine under the above-mentioned conditions points to the conclusion that the alkaloid is the dimethoxyl $(OCH_3)_2$ derivative of strychnine (Shenstone, C. J. 43, 101; Hanssen, B. 18, 1917), whilst the presence of a quinoline nucleus may be inferred from the nature of the products of the action of fused alkali.

Detection and estimation.—Brucine may be detected by means of the properties and reactions described above. It may be estimated in plants and in medicinal preparations by the methods described in connection with strychnine.

Curarine $C_{18}H_{35}N$, an alkaloid obtained from the Indian arrow-poison, known as 'curare' or 'urare,' an extract prepared from a number of plants of the genus *Strychnos*, chiefly from *S. toxifera*. It crystallises in colourless, four-sided prisms, which are hygroscopic and very soluble, both in water and alcohol, but less readily in chloroform and amyl alcohol, and very slightly soluble in ether. Neither the alkaloids nor its salts are stable; when exposed or heated in air they turn brown. Curarine has a very bitter taste, and is a violent poison; its physiological action consists chiefly in producing a complete paralysis of the motor nerves, without however appreciably impairing the excitability of muscle. On account of this property, 'curare' is largely used in physiological research. Sulphuric acid colours curarine deep blue or violet; nitric acid colours it deep red. With sulphuric acid and potassium bichromate it affords the same play of colours as strychnine (Ronlin a. Boussingault, A. Ch. [2] 39, 24; Preyer, Z. 1865, 381; Sachs, A. 191, 254).

From the more recent experiments of Böhm (C. C. 1887, 520) it appears that curarine is a yellow amorphous solid forming an amorphous platinichloride. The aqueous solution has a green fluorescence and a neutral reaction. When it is evaporated in presence of dilute hydrochloric acid, it furnishes crystalline needles, consisting of a decomposition product which is not poisonous. Besides curarine, Böhm finds in curare another alkaloid *curine*, which crystallises with difficulty; m.p. 160°. The platinichloride contains 19·3 p.c. of platinum, 1 p.c. more than the corresponding salt of curarine. Curine is not poisonous, and does not exhibit the characteristic physiological action of curarine. It combines with methyl iodide, however, to form the salt of a new base, which is highly poisonous and acts like curarine.

Taxine $C_{37}H_{52}NO_{10}$, the poisonous alkaloid contained in the seeds and leaves of the yew (*Taxus baccata*); m.p. 80–82°. Slightly soluble in water, soluble in alcohol, ether, and less readily in chloroform. A monacidic base, which forms salts difficult to crystallise (Marmé, Bl. 26, 417). An intense violet colouration is produced when the alkaloid is dissolved in concentrated sulphuric acid (Hilger a. Brande, B. 23, 464). Taxine is a narcotic poison.

THEOBROMINE AND THE ALKALOIDS OF TEA AND COFFEE.

The alkaloids belonging to this group are sharply distinguished by their chemical constitution from the large majority of the vegetable alkaloids. These bases are not pyridine or quinoline derivatives, but are di-ureides nearly related to uric acid, a substance hitherto only found in the animal organism.

Theobromine $C_7H_8N_4O_2$ occurs in cocoa beans (*Theobroma Cacao*), and in small quantity in certain kinds of tea. Cocoa beans usually contain 1–2 p.c. of theobromine; the nibs or shells of the bean contain about ·5 p.c.

Preparation.—Finely-powdered cocoa beans are exhausted with boiling water. Lead acetate solution is then added until no further precipitate is obtained. By this means tannic and other organic acids and colouring matter are removed. The filtrate is freed from lead by hydrogen sulphide, and evaporated to dryness. The residue is boiled with alcohol to dissolve the theobromine, which crystallises when the alcoholic solution is evaporated. Or the powdered beans may be mixed with about half their weight of quicklime, and the mixture boiled with alcohol (80 p.c.), which dissolves the theobromine (Schmidt a. Pressler, A. 217, 288; Dragendorff, B. 11, 1689).

Properties.—Crystals, which sublime when heated; m.p. 290–295° (Keller, A. 92, 71). Slightly soluble in water (1 in 1,600 at 17°; 1 in 148·5 at 100°) and in ether, rather more soluble in chloroform (1 in 105 at 62°). Very slightly soluble in absolute alcohol, more soluble in aqueous alcohol (rectified spirit, 1 in 47 at b.p.). Theobromine possesses both acid and feebly basic properties. It dissolves in aqueous alkalis, and the solution yields metallic derivatives which crystallise with difficulty and are decomposed by carbon dioxide, theobromine being liberated. The silver compound

$$(Ag.C_7H_7N_4O_2,1\tfrac{1}{2}H_2O)$$

is insoluble in water. It is produced as a semicrystalline precipitate when silver nitrate is added to a solution of theobromine in aqueous ammonia (Schmidt, A. 217, 282).

Theobromine acts as a monacidic base. It unites with acids, forming crystalline salts, which as a rule are decomposed by boiling with water (Schmidt a. Pressler, A. 217, 289).

Reactions.—Theobromine is precipitated by several of the alkaloid reagents, but not by Mayer's solution or by iodine. It is most easily detected by a reaction which is very similar to the murexide reaction for uric acid. The theobromine is first oxidised by warming it with chlorine water, or a drop of nitric acid, and evaporating to dryness. The residue consists chiefly of amalic acid (tetramethyl alloxantin $C_8(CH_3)_4N_4O_7$). The residue is coloured violet by potash and bright red by ammonia, owing to the formation of tetramethyl murexide. This reaction is very delicate, but it is also exhibited by the other alkaloids of this group.

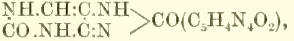
Theobromine does not unite with alkyl iodides. When it is heated with concentrated hydrochloric acid at 250°, or with baryta water, hydrolysis occurs, with formation of *carbon dioxide*, *ammonia*, *methylamine*, *methyl-amido-acetic acid* (sarcosine) and *formic acid*

$$C_7H_8N_4O_2 + 6H_2O$$
$$= 2CO_2 + 2NH_3 + NH_2CH_3 + C_3H_7NO_2 + H_2CO_2.$$

This reaction proves that theobromine contains two methyl groups, each united to a different atom of nitrogen.

Theobromine, unlike caffeïne, is not decomposed by warming with aqueous potash.

Chromic acid oxidises theobromine to *methyl parabanic acid*, *methylamine*, and *carbon dioxide*.

Theobromine is the dimethyl derivative of xanthine  $\begin{matrix}NH.CH{:}C.NH\\CO.NH.C{:}N\end{matrix}\!\!>CO(C_5H_4N_4O_2)$, a diureide whose composition differs from that of uric acid in containing an atom less of oxygen. Xanthine occurs in urine, and in various parts of the human body.

Theobromine may be prepared from xanthine by heating its lead or silver derivative with methyl iodide at 100° (Fischer, A. 215, 311).

Caffeïne or **Theïne** $C_8H_{10}N_4O_2$, the principal alkaloid of tea and coffee, in which it appears to occur as a salt of a variety of tannic acid. It is also found in Guarana, Paraguay tea, and in Kola-nuts. Coffee-beans are stated to contain an average of about 1 p.c. of caffeïne, and tea-leaves between 1–3 p.c. (Stenhouse, A. 89, 244; 102, 124; C. S. Mem. 1, 215; C. J. 9, 33). More recent determinations conducted with improved methods have shown that ordinary samples of tea-leaves contain from 3–4 p.c. of caffeïne, whilst commercial samples of coffee show a remarkable uniformity in containing rather less than 1·5 p.c. of the alkaloid (Paul a. Cownley, Ph. [3] 17, 565, 821, 921; 21, 61; Dvorkovitch, B. 24, 1945).

According to Kossel (Zeits. Physiol. Chem. 13, 298), tea also contains small quantities of *theophylline* (see below), *hypoxanthine* or *sarcine* ($C_5H_4N_4O$), *imido-sarcine* or *adenine* ($C_5H_5N_5$), and *xanthine* ($C_5H_4N_4O_2$), of which caffeïne is the trimethyl derivative.

Preparation.—Tea is heated for about an hour with four times its weight of boiling water, the solution is filtered and mixed with a weight of lime equal to that of the tea taken, and the mixture dried on the water-bath. The powdered residue is exhausted with boiling chloroform, which dissolves the caffeïne. The alkaloid is purified by crystallisation from alcohol or water (Cazeneuve a. Caillol, Bl. 27, 199; *cf.* Paul, Ph. [3] 21, 882). Or the methods described for the extraction of theobromine may be employed. Caffeïne may be extracted from coffee and the other substances which contain it by similar methods.

It should be remarked that no evidence has been adduced that the alkaloid extracted by these methods consists entirely of caffeïne. In the light of the recent work of Kossel, who has shown that, besides caffeïne, tea contains small quantities of at least four other nearly related bases, it is important that the residue of alkaloids should be more minutely examined. It is possible that the presence of small quantities of these other bases may account for the difference in physiological action, which has been recorded by several observers, between the caffeïne obtained from tea and that obtained from coffee.

Properties.—Silky needles, containing $1H_2O$ from water, anhydrous from alcohol, chloroform, and benzene. The hydrate loses its water at 100°, and the anhydrous caffeïne melts at 234–235° (Strecker, A. 118, 170; Dunstan a. Shepheard, C. J. 63, 197). Sublimes without decomposition. Soluble in cold water (1 in 90 at 15°), readily soluble in boiling water. Sparingly soluble in ether and absolute alcohol, more soluble in aqueous alcohol. Very soluble in chloroform (13 in 100 at 16°). The aqueous solution is neutral, and has a bitter taste.

Caffeïne is a very weak base. It dissolves in aqueous acids, acting as a monacidic base, forming salts which crystallise, but are decomposed on evaporation of their aqueous solutions, which, indeed, would seem to contain free alkaloid under ordinary conditions, since caffeïne can be extracted from them by shaking with chloroform. The salts of caffeïne with organic acids are particularly unstable. The double salts are more stable. The *aurichloride* ($B.HAuCl_4$) and *mercuric chloride compound* ($B.HgCl_2$) crystallise well (Nicholson, A. 62, 71; Schmidt, A. 217, 283; B. 14, 814). The aurichloride melts at 242·5, and is soluble in alcohol and to a smaller extent in water. It is decomposed when its aqueous solution is warmed with loss of two molecular proportions of hydrochloric acid, forming *aurichlor-caffeïne* ($C_8H_9(AuCl_2)N_4O_2$). This remarkable compound melts at 207° and is insoluble in water and alcohol. It dissolves in aqueous hydrochloric acid, reproducing the aurichloride (D. a. S.). Caffeïne does not unite directly with auric chloride, but it combines with auric potassium chloride, forming a red crystalline compound ($B.KAuCl_4$). This is precipitated by mixing a solution of caffeïne in chloroform with an alcoholic solution of potassium auric chloride. The salt melts at 208° and is resolved into its constituents on solution in water or acetone (Dunstan a. Shepheard, C. J. 63, 205).

For information concerning other caffeïne salts, the papers of Nicholson and Schmidt referred to above should be consulted.

Reactions. — Caffeïne is precipitated by several of the alkaloid reagents, but not by Mayer's solution or by a solution of iodine. It exhibits the murexide reaction (*v. Theobromine*), the oxidation being best effected by evaporating a solution of caffeïne in hydrochloric acid with a crystal of potassium chlorate.

Caffeïne combines with one molecular proportion of alkyl iodide. When heated with

concentrated hydrochloric acid in a closed tube, the alkaloid undergoes hydrolysis into *ammonia*, *carbon dioxide*, *methylamine*, *sarcosine*, and *formic acid*: $C_8H_{10}N_4O_2 + 6H_2O$
$= NH_3 + 2CO_2 + 2NH_2CH_3 + C_3H_7NO_2 + H_2CO_2$. This decomposition proves that caffeïne contains three methyl groups, each joined to a different nitrogen atom.

The action of alkalis (baryta water) on caffeïne is similar to that of hydrochloric acid, the same products being ultimately formed. A strong base *caffeïdine* ($C_7H_{12}N_4O$) is formed at first, but is subsequently decomposed. This base is derived from caffeïne by hydrolysis, one carbonyl group being split off as carbon dioxide and replaced by two atoms of hydrogen:

$$C_8H_{10}N_4O_2 + H_2O = CO_2 + C_7H_{12}N_4O.$$

On oxidation, preferably with hydrochloric acid and potassium chlorate, caffeïne furnishes *dimethyl-alloxan* and *methyl-urea*

$$C_8H_{10}N_4O_2 + O_2 + 2H_2O$$
$$= C_6H_8N_2O_5 + CONH_2NH(CH_3).$$

By further oxidation some of the dimethyl-alloxan is converted into *amalic acid* (*v. Theobromine*).

Caffeïne is the methyl derivative of theobromine, and consequently the tri-methyl derivative of xanthine. Caffeïne may be prepared by heating silver theobromine with methyl iodide (Strecker, A. 118, 170). For further information regarding the constitution of caffeïne *v.* Medicus, A. 175, 250; E. Fischer, A. 215, 314.

Estimation of caffeïne in tea and coffee.—A number of methods have been proposed for this purpose. Most of them consist in liberating the base by mixing the finely powdered material with aqueous alkali (about half its weight of lime or magnesia), and extracting the caffeïne from the dried and powdered mass with alcohol, chloroform, or benzene, the residue left on the evaporation of the solvent being weighed. Paul and Cownley (Ph. [3] 18, 417) prefer to use alcohol as the solvent, and recommend the following process as applicable for either tea or coffee. Five grms. of the powdered material are moistened with hot water and thoroughly mixed with one grm. of slaked lime, and the mixture dried on the water-bath. The powder is then extracted with boiling alcohol, the clear solution evaporated until the alcohol has been expelled, and the aqueous residue acidulated with dilute sulphuric acid and filtered. The caffeïne is then extracted from the acid solution by repeatedly shaking with chloroform, until nothing further is removed. The solution in chloroform is then shaken with dilute aqueous soda, washed with a little water, and distilled. The residue is weighed as pure caffeïne.

Vité (C. C. 1890, ii. 274), after having tried most of the methods which have been proposed, recommends the following plan: 5 grms. of finely powdered tea are extracted with three successive 100 c.c. of water by boiling for one hour. The liquid is concentrated to about 75 c.c., and mixed with freshly precipitated lead oxide and sand. The mixture is dried on the water-bath, powdered, and boiled with chloroform during three hours. The solution in chloroform is distilled, and the residue dissolved in hot water. The clear aqueous solution is evaporated on the water-bath, and the residue dried at 100° and weighed.

Dvorkovitch (B. 24, 1945) has conducted a similar inquiry, and describes a somewhat different method. His paper includes a large number of analyses of Chinese teas, which show a percentage of caffeïne ranging between about 2·5 and 3·5.

Since the amount of caffeïne contained in different commercial specimens of coffee berries is subject to but slight variation, the estimation of the caffeïne furnishes a useful indication of the presence of adulterants (Paul a. Cownley, Ph. [3] 17, 821, 921).

Theophylline $C_7H_8N_4O_2$, an isomeride of theobromine which occurs in small quantity in tea leaves (Kossel, Zeit. Phys. Chem. 13, 298; B. 21, 2164).

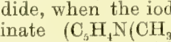
Preparation.—A large quantity of tea is exhausted by extraction with alcohol, and the solution evaporated to a syrup, from which the greater part of the caffeïne will crystallise out. This is removed, and the liquid residue diluted with water, acidulated with sulphuric acid. After having stood for some hours, the liquid is filtered, the filtrate made alkaline with ammonia, and precipitated by solution of silver nitrate. After the lapse of twenty-four hours the precipitate is filtered off, washed, and dissolved in a little warm nitric acid (rel. dens. 1·1). On cooling, the silver derivatives of sarcine and adenine crystallise out, leaving the silver theophylline dissolved. The acid filtrate is made alkaline with ammonia, and the precipitate of silver theophylline &c. collected, washed, suspended in water, acidulated with nitric acid, and decomposed by hydrogen sulphide. By evaporating the filtrate, crystals of xanthine separate, and afterwards the theophylline crystallises. A further quantity may be obtained from the mother-liquor by precipitation with mercuric nitrate and decomposition of the precipitate with hydrogen sulphide (Kossel, *l.c.*).

Properties.—Tabular crystals; m.p. 264°. Readily soluble in warm water. Slightly soluble in cold alcohol. Like theobromine, it affords the 'murexide' reaction, and in general its decomposition products are similar. When silver theophylline is heated with methyl iodide, caffeïne is formed.

Trigonelline $C_7H_9NO_2$, an alkaloid existing in fenugreek, the powdered seeds of *Trigonella Fœnum-græcum* (Jahns, B. 18, 2521; 20, 2840).

Properties.—Prismatic crystals, with $1H_2O$; m.p. 130°. Very soluble in water, slightly soluble in alcohol; very slightly soluble in ether, chloroform, and benzene. When heated with concentrated hydrochloric acid, it yields *methyl chloride* and *nicotinic acid* (β-pyridine carboxylic acid).

Jahns has proved that trigonelline is identical with the methyl-betaïne of nicotinic acid first prepared by Hantzsch (B. 19, 31). Nicotinic acid (C_5H_4NCOOH) is heated with potash and methyl iodide, when the iodo-methylate of methyl nicotinate ($C_5H_4N(CH_3I)CO.OCH_3$) is formed. On decomposition with silver oxide, this compound furnishes the betaïne



$$(C_5H_4N(CH_3)CO) \text{—} O$$

which is identical with trigonelline.

Ulexine $C_{11}H_{14}N_2O$ is found in *Ulex europæus* (Gerrard, Ph. [3] 17, 101, 229). It is identical with cytisine from laburnum (Partheil, Ar. Ph. 236, 667).

VERATRINE AND THE VERATRUM ALKALOIDS.

Cevadine or **Crystallised veratrine** $C_{32}H_{49}NO_9$ is the chief alkaloid of sabadilla or cevadilla seeds (*Asagræa officinalis, Schœnocaulon officinale, Veratrum Sabadilla*).

Preparation.—The finely powdered seeds are extracted with alcohol, containing 1 p.c. of tartaric acid. The acid liquid is evaporated, and diluted with water to precipitate resin. To the clear solution soda is added in slight excess, and the mixture completely extracted of alkaloid by repeatedly shaking with ether. The ethereal solution is mixed with light petroleum, and allowed to evaporate spontaneously. Crystals of cevadine separate from the syrup, and are recrystallised from their solution in alcohol. The remaining syrup contains the amorphous veratrine and cevadilline (Wright a. Luff, C. J. 33 338).

Sabadilla seeds contain about 0·1 p.c. of cevadine together with *sabadine* ($C_{29}H_{31}NO_8$), *sabadinine* ($C_{27}H_{45}NO_8$), and amorphous alkaloids (Merck, C. C. 1891, i. 363).

Commercial veratrine, which is an amorphous powder, appears to be a mixture of cevadine with amorphous alkaloids.

Properties.—Crystals; m.p. 182°, with decomposition. Nearly insoluble in water, soluble in alcohol and ether. Optically inactive. Acts as a monacidic base, forming salts, some of which are crystalline (Merck, A. 95, 200; Schmidt, A. 185, 224).

The *aurichloride* and the *mercurichloride* are characteristic crystalline compounds (Ahrens, B. 23, 2700).

Cevadine and its salts are poisonous.

Reactions.—When warmed with concentrated hydrochloric acid cevadine produces a fine red colour, which is a somewhat delicate test for the alkaloid. Concentrated sulphuric acid produces a carmine-red colouration, or, if the alkaloid is previously mixed with a little sugar, a blue.

The alkaloid unites with bromine to form a di-bromide and a tetra-bromide.

When allowed to stand with aqueous alkalis, or when heated with alcoholic potash, cevadine undergoes hydrolysis, furnishing *cevidine*

$$C_{27}H_{45}NO_9,$$

and *angelic acid* $C_5H_8O_2$. By the further action of alkali the angelic acid is converted into its isomeride *tiglic* or *methyl-crotonic acid*, whilst instead of cevidine, *anhydro-cevidine* or *cevine* ($C_{27}H_{45}NO_8$) is obtained (Wright a. Luff, C. J. 33, 338; 35, 405; Bosetti, Ar. Ph. [3] 21, 81; Ahrens, B. 23, 2700).

When oxidised by permanganate, cevadine yields *acetic* and *oxalic acids*, or when chromic acid is used, principally *acetic aldehyde* and *carbon dioxide*.

When the dry alkaloid is distilled, a *β-picoline* is obtained which is identical with that derived from strychnine.

Veratrine or **Amorphous veratrine** $C_{37}H_{53}NO_{11}$ is found in sabadilla seeds. On hydrolysis it yields *veratric acid* $C_9H_{10}O_4$ and *verine*

$$C_{28}H_{45}NO_8.$$

Verine closely resembles cevine.

Cevadilline or **Sabadilline** $C_{34}H_{53}NO_8$ is a second amorphous alkaloid occurring in sabadilla seeds.

Jervine $C_{26}H_{37}NO_3$ is an alkaloid contained in white hellebore (*Veratrum album*), which also contains the closely related alkaloids, *rubijervine* $C_{26}H_{43}NO_2$, *pseudo-jervine* $C_{29}H_{43}NO_7$, *proto-veratrine* $C_{32}H_{51}NO_{11}$, *proto-veratridine* $C_{26}H_{45}NO_8$, and, perhaps, *veratralbine* $C_{28}H_{43}NO_5$. The most poisonous of these alkaloids is protoveratrine (Wright a. Luff, C. J. 35, 405; Salzberger, Ar. Ph. 228, 462).

Similar alkaloids exists in green hellebore (*Veratrum viride*).

Penkschen (Ph. [5] 22, 265) has recently examined the alkaloids contained in *Veratrum album*, and has obtained somewhat different results. According to this observer, the chief alkaloids are: *jervine* ($C_{14}H_{22}NO_2$), *pseudo-jervine* ($C_{29}H_{49}NO_{12}$), *veratroidine* ($C_{32}H_{53}NO_9$).

Xanthine *v. Caffeïne* (*Theobromine and the alkaloids of tea and coffee*). W. R. D.

VENETIAN CHALK *v.* STEATITE.

VENETIAN LAKE. *Crimson lake v.* PIGMENTS.

VENETIAN RED. Ferric oxide.

VENETIAN WHITE. A white lead pigment containing a large percentage of barium sulphate.

VENICE TURPENTINE *v.* OLEO-RESINS.

VERA CRUZ ELEMI *v.* OLEO-RESINS.

VERANTIN *v.* MADDER.

VERATRIA FAT *v.* TALLOW.

VERATRINE *v.* VEGETO-ALKALOIDS.

VERATROL *v. Pyrocatechol*, art. PHENOL AND ITS HOMOLOGUES.

VERBENA OIL *v.* OILS, ESSENTIAL.

VERDIGRIS, VERT-DE-GRIS, VERT DE MONTPELIER. *Basic acetates of copper v.* ACETIC ACID.

VERDITER, GREEN AND BLUE, *v.* COPPER.

VERIDIAN. *Guignet's green v.* CHROMIUM.

VERJUICE. A kind of vinegar containing malic acid made from the juice of the crab-apple.

VERMILION *v.* MERCURY.

VERMILIONETTE. A red pigment made by adding eosin to white lead or zinc white.

VERT DE GUIGNET *v.* CHROMIUM.

VERT DIAMANT. Syn. for Victoria green, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

VERT ETINCELLE. VERT LUMIÈRE. *Methyl green v.* TRIPHENYLMETHANE COLOURING MATTERS.

VERT D'USÈBE. *Aldehyde green, Aniline green v.* TRIPHENYLMETHANE COLOURING MATTERS.

VESTORIEN *v.* EGYPTIAN BLUE; also ENAMELS.

VESUVINE *v.* AZO- COLOURING MATTERS.

VICTORIA BLUE. Chloride of phenyltetramethyl triamido-*α*-naphthyl diphenyl carbinol $C_{33}H_{32}N_3Cl$. A colouring matter patented by Caro a. Kern, and made by the Badische Anilin- und Soda-Fabrik. Forms a dark-blue crystalline powder, with coppery lustre; soluble in water with deep-blue colour. Solution becomes turbid on boiling, and gives a reddish precipitate. Dilute sulphuric acid changes the aqueous solution to green and then orange; on neutralising, the original colour is restored.

VICTORIA GREEN. *Benzaldehyde green v.* Triphenylmethane colouring matters.

VICTORIA ORANGE *v.* Victoria yellow.

VICTORIA YELLOW. *Gold yellow, Aniline orange, Saffron surrogate.* This colouring matter, introduced by Mettenzwei, under the name of *Victoria yellow* or *aniline orange* (W. J. 1869, 593), consists of the potassium or ammonium salt of a dinitrocresol (Martius and Wichelhaus, B. 2, 206; v. Sommaruga, B. 2, 579). It is prepared by heating cresol, boiling at about 195°, with three times its weight of sulphuric acid at 100°, until the product is soluble in water. After removing the excess of sulphuric acid by means of barium carbonate, the cresolsulphonic acid is converted into potassium salt, which in the dry state is nitrated by introducing it rapidly into about three times its weight of dilute nitric acid (sp. gr. = 1·2), and is then poured into water, neutralised with potassium carbonate, and the resulting potassium dinitrocresol crystallised out. Obtained in this way, the colouring matter is a mixture of the potassium salts of dinitro-ortho- and dinitro-para- cresol, and varies in colour according to the proportions of these. Thus Victoria yellow is yellowish in colour, and consists chiefly of the potassium salt of dinitro-orthocresol (m.p. = 86°), which crystallises in yellow needles (Wichelhaus, B. 7, 176; Piccard, B. 8, 685), while saffron surrogate is distinctly reddish in colour, and consists chiefly (80 p.c. according to Piccard) of the potassium salt of dinitroparacresol (m.p. = 84°), which crystallises in red needles (Armstrong and Field, C. N. 27, 318; Hofmann and v. Miller, B. 14, 567; Staedel, B. 14, 900, 906; Nölting and Salis, B. 14, 986).

Victoria yellow is soluble in water and dyes wool and silk orange, but owing to the fugitive nature of the colour is no longer employed for this purpose. Saffron surrogate is still used to some extent as a colouring matter for butter, margarine, vermicelli, cheese, &c. (Piccard), but this is to be deprecated, since Weyl's experiments show that the compound is poisonous (B. 20, 2835; 21, 512).

VIENNA BLUE. *Cobalt blue v.* Pigments.

VIENNA GREEN. *Emerald green v.* Pigments.

VIENNA PASTE. A mixture of lime and potash used as a caustic to extirpate malignant growths.

VIGORITE. A nitroglycerine preparation used as an explosive.

VINASSE *v.* Sugar.

VINE BLACK. *Blue black v.* Pigments.

VINEGAR *v.* Acetic acid.

VINEGAR, AROMATIC, *v.* Acetic acid; also Wood, destructive distillation of.

VINEGAR PLANT *v.* Acetic acid.

VIOLANILINE. A blue colouring matter belonging to the induline class; possibly identical with Coupier's blue, *v.* Indulines.

VIOLET DE PARIS or **VIOLET DIRECT.** *Methyl violet v.* Triphenylmethane colouring matters.

VIOLET IMPÉRIAL BLEU *v.* Triphenylmethane colouring matters.

VIOLET IMPÉRIAL ROUGE, VIOLET PHÉNYLIQUE. *Regina purple v.* Triphenylmethane colouring matters.

VIOLET SOLIDE. *Solid violet v.* Gallocyanine and Oxazine colouring matters.

VIOLET 5 B, 6 B, *v.* Triphenylmethane colouring matters.

VIOLET R and **R R** and **5 R.** *Hofmann's violet v.* Triphenylmethane colouring matters.

VIOLIN. An emetic substance contained in the common violet, supposed to be identical with emetine from ipecacuanha root.

VIOLINE or **VIOLEÏN.** A synonym for mauve or aniline purple.

VIRIDIAN. Hydrated chromium sesquioxide, *v.* Chromium.

VIRIDINE *v.* Alkali green.

VITELLIN *v.* Albuminoids.

VITRIFIABLE PIGMENTS *v.* Pottery; also Porcelain.

VITRIOL (*vitrum*, 'glass'). An old name for a sulphate, and still frequently applied to the sulphates of certain common metals on account of their vitreous lustre, *e.g.* white or zinc vitriol $ZnSO_4.7H_2O$; blue or copper vitriol $CuSO_4.5H_2O$; green or iron vitriol $FeSO_4.7H_2O$; red or cobalt vitriol $CoSO_4.7H_2O$. Basic ferric or ferroso-cupric sulphates obtained in the extraction of copper sulphate from ferruginous minerals are known as Admont, Bayreuth, Salzburg vitriols, &c.

VITRIOL, OIL OF. *Vitriolic acid.* Concentrated sulphuric acid.

VITRIOL STONE and **COLCOTHAR.** Vitriol is the important material from which the so-called fuming or Bohemian sulphuric acid is manufactured, and it is obtained from the rock known as vitriol slate ('vitriolschiefer') in the following manner. Large masses of pyritous slate (which belongs to the Silurian formation, and consists of a quartzose matrix containing pyrites, carbon, and clay) are exposed to the weathering action of the atmosphere for three years. The products of oxidation so formed are ferrous sulphate and sulphuric acid, which latter acts energetically upon the clay; and finally, aluminium sulphate and other sulphates are yielded. The ferrous sulphate at first formed becomes by oxidation ferric sulphate, which, together with the aluminium sulphate, is the principal product of the weathering of the vitriol slate. Ferrous sulphate remains only in small quantities. The next operation is lixiviation of the mass with water, after which the liquor obtained is concentrated to a density of 40°B., and finally evaporated in pans until, on cooling, a crystalline cake of vitriol stone is obtained. The vitriol stone is now calcined, in order to remove the greater part of its water. The resulting product, when heated to a high temperature in clay retorts, yields sulphuric anhydride; and a residue, termed colcothar, remains in the retorts. The composition of vitriol stone and colcothar will be seen from the following analysis:—

Vitriol stone. Fe_2O_3 20·07, Al_2O_3 4·67, FeO 0·64, MnO traces, CaO 0·14, MgO 0·39, K_2O 0·07, Na_2O 0·05, CuO 0·10, SiO_2 0·10, P_2O_5 traces, SO_3 40·51, As traces, H_2O 32·58–99·32, or combining acid oxides and bases: $Fe_2(SO_4)_3$ 50·17, $Al_2(SO_4)_3$ 11·94, $FeSO_4$ 1·35, $MgSO_4$ 1·17, $CaSO_4$ 0·33, $CuSO_4$ 0·20, K_2SO_4 0·13, Na_2SO_4 0·11, H_2SO_4 1·49, MnO, As, and P_2O_5 traces, SiO_2 9·10, OH_2 3·31–99·29.

Colcothar. Fe_2O_3 7·62, Al_2O_3 12·53, MgO 3·23, CaO 0·82, SO_3 5·17, SiO_2 1·17, CuO 0·20, H_2O

1·30–99·04 (F. Stolba, B. Königl. Böhm. Gesells. 1885; S. C. I. 6, 30).

VIVIANITE. *Ferrous phosphate* v. Iron.

VOLBORTHITE *v.* Vanadium.

VOLGERITE. *Antimony tetroxide* v. Antimony.

VOLUMENOMETER *v.* Specific gravity.

VRAIC. *Varech.* The French name for kelp, *v.* Iodine.

VULCANITE *v.* Indiarubber or Caoutchouc. Also applied to a nitroglycerin explosive.

VULCAN POWDER *v.* Explosives.

VULPIC or **VULPULIC ACID** *v.* Lichens.

VULPINITE. A variety of anhydrite mixed with silica. That from Vulpino near Bergamo, known as the *Marmo Bardiglio di Bergamo*, takes a fine polish and is used for ornamental purposes.

W

WAD *v.* Manganese.

WALCHOVITE *v.* Resins.

WALNUT HUSKS (*Brous des noix*, Fr.) are employed by the French dyers to give dun colours. The green shells contain *juglone* or *hydroxy-*[α]*-naphthaquinone*; *v.* Naphthalene.

WALNUT OIL *v.* Oils, fixed, and fats.

WASH. The name given to the fermented wort of the distiller.

WATER GLASS. *Soluble glass v.* Glass, vol. ii. 224.

WATER. There is no substance of greater importance on the earth than water, which is absolutely indispensable to both animal and vegetable life, which is the cause of many of the most striking phenomena in nature, and which is employed for countless purposes by man. Its distribution is as wide as that of the air itself, whilst the absolute amount in which it occurs on the earth is enormously greater. In a perfectly pure state it is never met with in nature, and can only be obtained by the most refined operations; but the scope of the present article embraces rather the impurities present in the several kinds of water, and the discussion of their significance in connection with the various uses to which water is applied. The impurities in water are derived from the materials—solid, liquid, or gaseous—with which it comes in contact, and they may be present either in suspension or in solution or in both; but owing to the great solvent power of water all its natural forms contain matters in solution, whilst in many cases matters in suspension may be practically wholly absent. Inasmuch, therefore, as the interest attaching to different waters depends upon the impurities they contain, and these are dependent upon the matters with which they have been in contact, it is most convenient to classify waters according to their origin.

1. *Rain-water, snow, hail, dew, and hoar-frost.* All these forms of water are obtained by the condensation of the aqueous vapour which is invariably more or less abundantly present in the air. The amount of aqueous vapour which can be contained in a given volume of air is solely dependent upon the temperature—or rather the '*tension of aqueous vapour*,' which rises with the temperature, as indicated in the following table:—

Tension of aqueous vapour for each $\frac{1}{10}$th degree Centigrade, from 0° to 30°C. (Regnault).

Temp. C.	Tension in mm. of mercury	Temp. C.	Tension in mm. of mercury	Temp. C.	Tension in mm. of mercury	Temp. C.	Tension in mm. of mercury
0	4·6	2·3	5·4	4·6	6·4	6·9	7·4
·1	4·6	·4	5·5	·7	6·4	7·0	7·5
·2	4·7	·5	5·5	·8	6·4	·1	7·5
·3	4·7	·6	5·5	·9	6·5	·2	7·6
·4	4·7	·7	5·6	5·0	6·5	·3	7·6
·5	4·8	·8	5·6	·1	6·6	·4	7·7
·6	4·8	·9	5·6	·2	6·6	·5	7·8
·7	4·8	3·0	5·7	·3	6·7	·6	7·8
·8	4·8	·1	5·7	·4	6·7	·7	7·9
·9	4·9	·2	5·8	·5	6·8	·8	7·9
1·0	4·9	·3	5·8	·6	6·8	·9	8·0
·1	5·0	·4	5·8	·7	6·9	8·0	8·0
·2	5·0	·5	5·9	·8	6·9	·1	8·1
·3	5·0	·6	5·9	·9	7·0	·2	8·1
·4	5·1	·7	6·0	6·0	7·0	·3	8·2
·5	5·1	·8	6·0	·1	7·0	·4	8·2
·6	5·2	·9	6·1	·2	7·1	·5	8·3
·7	5·2	4·0	6·1	·3	7·1	·6	8·3
·8	5·2	·1	6·1	·4	7·2	·7	8·4
·9	5·3	·2	6·2	·5	7·2	·8	8·5
2·0	5·3	·3	6·2	·6	7·3	·9	8·5
·1	5·3	·4	6·3	·7	7·3	9·0	8·6
·2	5·4	·5	6·3	·8	7·4	·1	8·6

Tension of aqueous vapour (continued).

Temp. C.	Tension in mm. of mercury	Temp. C.	Tension in mm. of mercury	Temp. C.	Tension in mm. of mercury	Temp. C.	Tension in mm. of mercury
9·2	8·7	14·4	12·2	19·6	17·0	24·8	23·3
·3	8·7	·5	12·3	·7	17·1	·9	23·4
·4	8·8	·6	12·4	·8	17·2	25·0	23·5
·5	8·9	·7	12·5	·9	17·3	·1	23·7
·6	8·9	·8	12·5	20·0	17·4	·2	23·8
·7	9·0	·9	12·6	·1	17·5	·3	24·0
·8	9·0	15·0	12·7	·2	17·6	·4	24·1
·9	9·1	·1	12·8	·3	17·7	·5	24·3
10·0	9·2	·2	12·9	·4	17·8	·6	24·4
·1	9·2	·3	12·9	·5	17·9	·7	24·6
·2	9·3	·4	13·0	·6	18·0	·8	24·7
·3	9·3	·5	13·1	·7	18·2	·9	24·8
·4	9·4	·6	13·2	·8	18·3	26·0	25·0
·5	9·5	·7	13·3	·9	18·4	·1	25·1
·6	9·5	·8	13·4	21·0	18·5	·2	25·3
·7	9·6	·9	13·5	·1	18·6	·3	25·4
·8	9·7	16·0	13·5	·2	18·7	·4	25·6
·9	9·7	·1	13·6	·3	18·8	·5	25·7
11·0	9·8	·2	13·7	·4	19·0	·6	25·9
·1	9·9	·3	13·8	·5	19·1	·7	26·0
·2	9·9	·4	13·9	·6	19·2	·8	26·2
·3	10·0	·5	14·0	·7	19·3	·9	26·4
·4	10·1	·6	14·1	·8	19·4	27·0	26·5
·5	10·1	·7	14·2	·9	19·5	·1	26·7
·6	10·2	·8	14·2	22·0	19·7	·2	26·8
·7	10·3	·9	14·3	·1	19·8	·3	27·0
·8	10·3	17·0	14·4	·2	19·9	·4	27·1
·9	10·4	·1	14·5	·3	20·0	·5	27·3
12·0	10·5	·2	14·6	·4	20·1	·6	27·5
·1	10·5	·3	14·7	·5	20·3	·7	27·6
·2	10·6	·4	14·8	·6	20·4	·8	27·8
·3	10·7	·5	14·9	·7	20·5	·9	27·9
·4	10·7	·6	15·0	·8	20·6	28·0	28·1
·5	10·8	·7	15·1	·9	20·8	·1	28·3
·6	10·9	·8	15·2	23·0	20·9	·2	28·4
·7	10·9	·9	15·3	·1	21·0	·3	28·6
·8	11·0	18·0	15·4	·2	21·1	·4	28·8
·9	11·1	·1	15·5	·3	21·3	·5	28·9
13·0	11·2	·2	15·6	·4	21·4	·6	29·1
·1	11·2	·3	15·7	·5	21·5	·7	29·3
·2	11·3	·4	15·7	·6	21·7	·8	29·4
·3	11·4	·5	15·8	·7	21·8	·9	29·6
·4	11·5	·6	15·9	·8	21·9	29·0	29·8
·5	11·5	·7	16·0	·9	22·1	·1	30·0
·6	11·6	·8	16·1	24·0	22·2	·2	30·1
·7	11·7	·9	16·2	·1	22·3	·3	30·3
·8	11·8	19·0	16·3	·2	22·5	·4	30·5
·9	11·8	·1	16·4	·3	22·6	·5	30·7
14·0	11·9	·2	16·6	·4	22·7	·6	30·8
·1	12·0	·3	16·7	·5	22·9	·7	31·0
·2	12·1	·4	16·8	·6	23·0	·8	31·2
·3	12·1	·5	16·9	·7	23·1	·9	31·4

If, then, the atmosphere has become saturated with aqueous vapour at any given temperature and is then cooled below that temperature, the excess of aqueous vapour will condense, according to circumstances, as rain, hail, snow, mist, dew, or hoar-frost. All these forms of water having been only in contact with the air and not with the earth are characterised by the small proportion of solid matter which they contain, although the amount found, especially in the vicinity of towns, is often considerably greater than would be anticipated, and the rain-water falling in the neighbourhood of the sea is often mixed to a considerable extent with sea-spray, which with favourable winds is carried many miles inland. The most careful experiments on the composition of rain-water have been made at Rothamstead, Herts, the rain being there collected in a specially-constructed gauge placed in a field at a distance of twenty-five miles from London. In the following table are recorded the maximum, minimum, and average proportions of each of the several ingredients determined in no less than seventy-one samples of rain-water collected in this gauge (Sixth Report of River Pollut. Commiss. 1874).

Seventy-one samples of Rain-water collected at Rothamstead, 1869–1872.

(Results of Analysis expressed in parts per 100,000.)

——	Total solid impurity	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum . .	0·62	·021	·003	·005	0	0	0
Maximum . .	8·58	·372	·121	·155	·044	1·65	1·7
Average . .	3·42	·095	·021	·049	·007	·33	·5
Rain-water collected at Land's End, Cornwall, Jan. 2, 1873	42·80	·131	·034	0	·020	21·8	10·0
Rain-water collected near Hyde Park, London, Nov. 8, 1873	2·76	·383	·040	·210	·008	·5	1·1

It is thus seen that the composition of rain-water, even in the open country, is liable to very great fluctuations, and that the amount of impurity, both mineral and organic, is occasionally surprisingly large. The amount of organic impurity in dew and hoar-frost is even still greater owing to these forms of water being condensed out of the lowest and most-contaminated couches of the atmosphere. Thus

Seven samples of Dew and Hoar-frost, Rothamstead, 1869 *and* 1870.

(Results of Analysis expressed in parts per 100,000.)

——	Total solids	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum . .	2·61	·195	·026	·130	0	·35	1·3
Maximum . .	8·00	·450	·196	·280	·050	·80	2·5
Average . .	4·87	·264	·076	·198	·023	·53	1·9

It must not, however, be supposed that the above figures for rain-water give any idea of the composition of the water to be found in rain-water tanks and cisterns; such water is generally much contaminated by storage, besides containing the washings of the roofs and gutters from which it has been collected.

Two other impurities, not referred to above, which are generally present in the rain-water and snow of towns are sulphurous and sulphuric acids derived from the combustion of coal. Thus Angus Smith found in the rain-water of London 2·05, of Liverpool 3·96, in that of Manchester 4·48, and in that of Glasgow 7·02 parts per 100,000 of sulphuric acid, to a considerable extent in the free state. Very striking is the property which snow has of absorbing the sulphurous acid from the air. Thus Sendtner found freshly-fallen snow in Munich to contain ·7 part sulphuric acid (SO_3) per 100,000, on the following day 1·76 parts, after ten days 6·22 parts, and after sixteen days 9·18 parts. The presence of this free acid in the rain-water of towns is, of course, not only highly detrimental to vegetation, but also to sculptures and buildings in which marble or limestone are employed. In the same way the proportion of ammonia increases in the snow after lying on the ground (Wagner, Technologie, 305).

For the volume and nature of the gases dissolved in rain-water see p. 964.

2. *Upland surface water.* This, of the various kinds of terrestrial water, most nearly approaches in composition that of the atmospheric waters dealt with in the last section. It is, in point of fact, rain-water which has undergone minimum contact with the earth, although in consequence of the powerful solvent action of water even this contact is sufficient to impart to the water in many cases such proportions of dissolved matter as are never found in rain-water. The amount and nature of these ingredients depends, of course, mainly upon the kind of soil over which the water has travelled, and consequently it becomes convenient to further sub-divide this class according to the geological character of the ground from which the upland surface water has been obtained.

In the following tables are recorded the maximum, minimum, and average amounts of impurity found in the examination of a most extensive series of samples, and published in the Sixth Report of the Rivers Pollution Commission, 1874. The waters are in all cases principally derived from land not under cultivation, so as to represent the characters naturally acquired by water passing over the various geological formations.

I.—*Waters from non-calcareous strata.*

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(*a*) *Upland surface water from Igneous rocks.*[1]										
Maximum. . .	12·70	·582	·071	·004	·029	·073	2·10	·4	5·7	5·9
Minimum . . .	1·52	·074	·013	0	0	·014	·35	0	·8	·8
Average (18 samples)	5·15	·278	·033	·001	·002	·035	1·13	·1	2·0	2·1
(*b*) *Upland surface water from Metamorphic, Cambrian, Silurian, and Devonian rocks.*[2]										
Maximum. . .	12·48	1·059	·076	008	·043	·110	3·35	1·8	6·9	6·9
Minimum . . .	2·14	·042	·001	0	0	·002	·52	0	·3	·4
Average (81 samples)	5·12	·293	·024	·002	·006	·031	·92	·3	2·5	2·5
(*c*) *Upland surface water from Yoredale and millstone grits and non-calcareous portion of the coal measures.*[3]										
Maximum. . .	15·00	1·457	·103	·024	·042	·116	1·59	3·7	8·1	8·7
Minimum . . .	4·58	·033	0	0	0	·012	·65	0	·9	·9
Average (47 samples)	8·75	·377	·033	·003	·010	·050	1·05	·4	4·3	4·7
(*d*) *Upland surface water from Lower London Tertiaries and Bagshot beds.*										
Maximum. . .	13·14	·439	·056	·012	·020	·086	2·60	·9	5·6	5·6
Minimum . . .	5·92	·282	·039	0	0	·039	1·24	0	1·8	1·8
Average (3 samples) .	8·40	·379	·048	·004	·007	·058	2·06	·3	3·5	3·8

[1] All soft and peaty. Generally turbid, and of a yellowish or even brownish colour.

[2] This water is also generally peaty, and often turbid and coloured. Owing to the large area of these rocks exposed they form some of the most important gathering grounds, especially in Scotland.

[3] Soft, but generally turbid, peaty, and of a yellow or brownish colour.

II.—*Waters from calcareous strata.*

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(*a*) *Upland surface water from Silurian and Devonian rocks.*[1]										
Maximum. . .	14·46	·475	·046	0	·055	·080	1·62	3·5	9·6	9·6
Minimum . . .	12·26	·103	·008	0	0	·016	·83	0	5·2	7·5
Average (3 samples, all from Scotland)	13·71	·301	·026	0	·021	·047	1·20	1·2	7·4	8·6
(*b*) *Upland surface water from mountain limestone.*[2]										
Maximum. . .	23·40	·812	·097	·002	·042	·097	1·59	9·3	10·6	14·6
Minimum . . .	12·45	·218	·023	0	0	·024	·92	1·7	4·3	9·8
Average (7 samples) .	17·07	·370	·047	·001	·011	·059	1·24	5·7	7·0	12·7
(*c*) *Upland surface water from calcareous portion of coal measures.*[3]										
Maximum. . .	77·36	·856	·089	·010	·061	·122	4·85	11·6	13·6	25·0
Minimum . . .	10·20	·082	·001	0	0	·014	·84	0	3·0	6·2
Average (26 samples)	22·79	·346	·037	·003	·016	·056	1·52	4·0	8·3	12·3
(*d*) *Upland surface water from Lias, New Red, and Conglomerate Sandstone.*										
Maximum. . .	26·32	·506	·075	·008	·034	·100	2·00	16·0	12·9	24·8
Minimum . . .	11·08	·186	·020	0	0	·022	·99	2·9	3·1	6·0
Average (8 samples) .	18·92	·300	·042	·002	·012	·056	1·50	7·8	6·3	14·0
(*e*) *Upland surface water from magnesian limestone.*[4]										
Ripon, the Kex Beck, 8 miles from source, Jan. 27, 1874 .	17·84	·172	·036	·001	0	·037	1·40	6·4	8·3	14·7
(*f*) *Upland surface water from Oolites.*[5]										
The Frome, above Woodlands Mill, Somersetshire, March 10, 1870.	17·46	·326	·025	·004	·042	·070	1·55	6·6	5·8	12·4

[1] Owing to the compact nature of the limestone in these old formations, the hardness is very moderate.

[2] Hardness not excessive, but large amount of organic matter (peaty), rendering the waters coloured and unpalatable.

[3] Of very variable character; generally of only moderate hardness, but containing much peaty matter, and hence coloured and unpalatable.

[4] Slightly turbid.

[5] Slightly turbid. Owing to the porous nature of Oolite formation, surface water is very rare.

The above analyses show that the upland urface waters generally contain any considerble amount of dissolved matters only when hey are derived from calcareous strata. The rganic matter is subject to great variations, but vill in every case be seen to contain only a very mall proportion of nitrogen in comparison with he carbon, indicating that the organic subtances present are of vegetable and not of nimal origin, which is further attested by the lmost entire absence of ammonia, nitrates, and itrites, all of which, when present in amount eyond that in which they occur in rain-water, re nearly exclusively derived from the decomosition of animal matters. The chlorine is also, lmost without exception, low, the upland gatherig grounds being generally beyond the reach of ea-spray and not receiving the liquid excrements f man and animals, which are particularly rich in chlorides, whilst from their mere surface contact with the soil they have not extracted any considerable quantities of the salts present in the latter, as is the case with spring- and well-water.

3. *Surface water derived from cultivated land.* This includes the great body of river-waters, inasmuch as practically all streams flow through and receive accessions from land under cultivation before reaching the sea. The composition of such waters is very varied, depending as it does upon many local circumstances, and being liable to great fluctuations at different seasons of the year. This group may, however, be conveniently divided into two sub-groups, according as the water is derived from calcareous or non-calcareous districts. The following results of analyses of British waters of this description are compiled from the Sixth Report of the Rivers Commission 1874 :—

Surface waters from cultivated land.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(a) Water from non-calcareous districts.[1]										
Maximum . .	18·10	1·124	·112	·056	·258	·393	2·80	4·6	8·0	10·1
Minimum . .	5·26	·125	0[2]	0	0	·017	·70	0	1·8	2·1
Average (31 samples)	9·52	·276	·034	·007	·089	·128	1·49	·6	4·3	4·9
(b) Water from calcareous districts.[3]										
Maximum . .	110·40	1·338	·307	·030	1·005	1·096	12·75	26·3	42·1	67·3
Minimum . .	13·22	·069	·009	0	0	·033	0·54	0	2·1	7·8
Average (144 samples)	30·08	·268	·053	·005	·257	·314	2·24	12·4	8·2	20·6

[1] Usually turbid, organic matter generally moderate in amount, but partially of animal origin.

[2] This result is extremely improbable, more especially as the particular water in question (a sample of the water applied to Bury and Radcliffe, Lancashire) contained ·229 organic carbon, ·032 ammonia, and ·066 nitrogen as nitrates nd nitrites.

[3] Generally turbid, the organic matter is much the same in amount as in the water from non-calcareous districts, but enerally more nitrogenous, in consequence of calcareous soils being usually under higher cultivation than non-calcareos ones. The total combined nitrogen is also for the same reason considerably greater, and the hardness is, of course, ery much higher.

It will be seen that these surface waters erived from cultivated land differ still more aterially from the original rain-water than o the upland surface waters of the previous roup.

In connection with the effect of cultivated nd upon the water which comes in contact vith it, it is particularly instructive to note the ature of the water which drains from such land, s this throws the most important light upon he composition of subterranean waters (from springs and wells), which will be considered below. An elaborate series of experiments on this subject was jointly undertaken by the Rivers Pollution Commissioners and Messrs. Lawes and Gilbert some twenty years ago.

Firstly, in the following table is recorded the composition of the water obtained from drain-pipes placed from 18 inches to 5 feet below a plot of land at Rothamstead which had remained both unmanured and uncropped for a period of eleven to fifteen years :—

Composition of water from land unmanured and uncropped for eleven to fifteen years.[1]

(6th Rep. Riv. Com. p. 62.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	63·28	·235	·116	·026	4·936	4·981	3·80	7·2	11·9	16·6
Minimum . .	18·00	·096	·026	0	·607	·654	·60	·3	3·2	3·5
Average (15 samples distributed over four years) .	32·06	·154	·053	·006	2·195	2·253	1·65	4·1	8·5	12·6

[1] The samples varied from clear to turbid.

From this table it will be seen that the conversion of the original nitrogenous organic matter in the soil into mineral products is a very slow process, large quantities of nitrates being still present in the drainage waters after the lapse of so many years (*v.* NITRIFICATION).

It is interesting to compare with the above the composition of the water draining from a plot of land unmanured for sixteen to twenty-one years, but continuously bearing an annual wheat crop during that time:—

Composition of water from land unmanured for sixteen to twenty-one years, but continuously bearing wheat crops. (6th Rep. Riv. Com. p. 60.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	48·40	·242	·058	·006	2·268	—	3·80	14·1	22·4	32·7
Minimum . .	13·80	·099	·010	0	0	—	·80	8·9	3·9	13·5
Average (11 samples distributed over five years) .	24·96	·170	·034	·002	·645	—	1·37	10·8	8·4	19·2

As might have been anticipated, the proportions of ammonia and nitrates finding their way into the drainage water in this case were much less, and in the summer months during the growth of the crop the amount of this mineral nitrogen found in the drainage water was practically *nil.*

We will, in the next place, compare with the above the composition of the drainage water from land which had annually been manured with 14 tons of farmyard manure per acre over a period of twenty-four to twenty-nine years, and bearing wheat continuously during that time:—

Composition of drainage water from land manured with 14 *tons farmyard manure per acre for twenty-four to twenty-nine years.* (6th Rep. Riv. Com. p. 58.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	51·20	1·243	·335	·052	2·592	2·754	3·35	12·1	20·6	32·1
Minimum . .	14·00	·181	·036	0	·082	·130	·60	1·4	5·4	8·7
Average (13 samples over five years)	25·90	·519	·115	·009	·528	·665	1·30	6·8	8·6	15·4

Thus the difference between the drainage waters from the unmanured and manured land is not nearly so great as might have been expected, being principally confined to the larger proportion of organic matter found in the latter.

The above results may also be profitably compared with those obtained in the analysis of a large number of samples of the drainage water from the sewage farms at Barking (London), Aldershot, Bedford, Romford, Altrincham, Norwood, and Croydon, in all of which the town sewage is, or was, applied to land, with the double object of purifying the sewage and deriving a profit out of the crops raised. Thus:—

Composition of drainage water from sewage farms. (6th Rep. Riv. Com. pp. 55–57.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	103·00	2·160	·517	1·366	6·499	6·833	13·40	36·9	39·3	56·6
Minimum . .	18·60	·108	·034	·005	0	·069	2·15	0	3·9	3·9
Average (72 samples)	64·02	·982	·191	·388	·756	1·266	6·36	17·6	15·4	33·0

It will thus be seen that the drainage water from such sewage farms is generally far richer in both organic and inorganic impurities than the water draining from either manured or unmanured land, the passage of the water through the ground being in the latter case a much slower one, and thus allowing time for more perfect purification by soil and plants. Occasionally, as indicated by the above minimum results, the drainage water from sewage farms is most remarkably free from impurities. A much purer drainage water is often yielded in the careful intermittent downward filtration of sewage through suitable land, as is indicated by the following results obtained by such treatment of the sewage of Merthyr Tydfil:—

Composition of drainage water from intermittent filters. (6th Rep. Riv. Com. p. 57.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . .	36·28	·249	·056	·095	·341	·433	3·25	12·4	11·7	22·4
Minimum . .	31·88	·103	·012	·025	·194	·226	2·60	7·2	8·1	17·1
Average (6 samples)	33·93	·156	·032	·063	·269	·352	2·84	10·0	9·7	19·7

These are chemically almost indistinguishable from drinking water, so perfect is the purification effected in traversing a few feet of porous soil.

The knowledge thus gained of the composition of waters draining from cultivated land becomes of special value in studying the nature of the next group of waters (shallow well water) upon which such a large part of the population in villages and country districts depends.

4. *Shallow well water.* It has been estimated that about twelve millions of the inhabitants of Great Britain are supplied with water for domestic purposes from shallow wells. This class of water is, above all others, liable to the most serious contamination with sewage and other refuse animal matters, inasmuch as such wells for domestic supply are almost invariably sunk in the immediate vicinity of human dwellings, and very frequently within a few feet of the cesspool receiving their drainage. It is just these waters also which have been most frequently found guilty of causing serious outbreaks of typhoid fever amongst the persons using them. In consequence of the great practical interest attaching to these waters, their composition will be considered in connection with the principal geological formations upon which such shallow wells may be sunk.

The series of results recorded on the next page affords a remarkably complete picture of the composition of shallow well waters as met with in Great Britain. It will be at once apparent within what very wide limits the composition of these waters varies, even when derived from one and the same geological formation, which is due to their being not generally an aqueous extract of a soil in its natural condition, but of ground which has received all manner of additions, and which is often saturated with sewage and other animal refuse. In consequence of the extraordinary oxidising power of soil, the organic matter of this refuse is not unfrequently almost entirely destroyed before reaching the wells, and even the ammonia, which is one of the first products of its decomposition, has often entirely disappeared, having generally become converted into nitrates and nitrites. Of nitrates and nitrites these shallow well waters generally contain some, and often a most astonishingly large amount, which thus, together with the ammonia, testify to the water having previously been in contact with nitrogenous organic matter which has subsequently undergone destruction. It is the custom of some water analysts to designate this evidence afforded by the presence of mineral nitrogen (ammonia, nitrates, and nitrites) as '*previous sewage contamination*'; but the term is open to grave objections, inasmuch as water may lose this mineral nitrogen through the action of micro-organisms and other plant-life in the soil, and thus become stripped of its history, which may be as bad, and worse, than that of a water containing an abundance of nitrates or ammonia. In shallow well waters, even when the organic matter is only small in amount, it is generally highly nitrogenous, pointing to its probable animal origin, and in some exceptional cases the organic nitrogen found is actually in excess of the carbon. These waters, which are generally suspicious from the presence of mineral nitrogen, become in the highest degree dangerous when the proportion of organic matter is large also, although they are generally, notwithstanding the abundance of such revolting impurity, clear, palatable, and usually preferred by unwary consumers to waters containing a far smaller proportion of innocuous vegetable organic matter.

5. *Deep well waters.* It has been found convenient to distinguish for sanitary purposes between waters which are obtained from comparatively shallow wells and those which are derived from wells or bore-holes of, say, upwards of 100 feet in depth, and sometimes reaching to the profound distance of more than 1,000 feet below the surface of the earth. The presumption is in favour of waters obtained from such a depth having undergone very perfect filtration through porous strata, and consequently it is not usual to view the evidence of previous contact with animal matters which is afforded by the presence of mineral nitrogen with so much suspicion as in the case of the waters from the shallower wells. The great efficiency of the filtration which most of these deep well waters have undergone is attested both by their extraordinary freedom from organic matter, and by their almost absolute freedom from every kind of suspended material, whether organic or inorganic (see, for the bacteriological examination of water, the table on page 992). In consequence of the excellent water obtainable from such deep wells, they have been multiplied enormously during the past thirty years, so that at the present time not only are many towns (including a part of London) and villages supplied from this source, but also nearly all larger breweries and many private establishments in which a premium is put upon a pure water supply. In some cases these deep wells are of the kind

Shallow well waters.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Gneiss and Silurian rocks[1] (6th Rep. Riv. Com. p. 69).										
Maximum . .	100·20	·362	·110	·625	2·465	3·090	17·00	22·3	19·2	41·5
Minimum . .	6·32	·027	·003	0	·033	·040	·90	0	3·3	3·4
From Devonian rocks[2] (29 samples analysed).										
Maximum . .	105·20	·794	·172	·630	4·197	4·261	17·00	18·3	47·8	55·7
Minimum . .	12·16	·004	·003	0	·033	·039	1·60	0	3·2	5·0
From Yoredale and millstone grits[3] (20 samples analysed).										
Maximum . .	133·60	·859	·216	·010	5·100	5·200	13·90	37·2	65·1	90·0
Minimum . .	5·92	·039	·007	0	·006	·013	·65	0	2·9	2·9
From coal measures[4] (44 samples analysed).										
Maximum . .	220·92	1·200	·169	·170	10·102	10·262	29·00	28·2	112·6	140·8
Minimum . .	9·40	·024	·007	0	0	·015	·99	0	1·4	3·4
From mountain limestone and magnesian limestone[5] (9 samples analysed).										
Maximum . .	108·88	·190	·070	·002	4·812	4·884	13·35	40·1	48·5	88·6
Minimum . .	45·84	·037	·010	0	·527	·549	2·40	18·3	21·8	40·7
From New Red Sandstone[6] (87 samples analysed).										
Maximum . .	240·20	2·349[7]	·346[7]	·620	14·717	15·333	39·00	52·0	99·6	127·1
Minimum . .	20·64	·029	·009	0	0	·027	1·40	0	3·8	17·1
From Lias[8] (38 samples analysed).										
Maximum . .	306·85	1·792	·298	·152	19·858	20·123	40·50	40·1	111·0	116·9
Minimum . .	49·48	·052	·023	0	0	·033	1·75	0	1·2	2·7
From Oolites[9] (25 samples analysed).										
Maximum . .	269·60	2·662	·531	·240	12·220	12·508	44·50	42·6	55·9	78·9
Minimum . .	31·00	·041	·008	0	0	·178	1·23	10·8	3·1	23·0
From Upper and Lower Greensand and Wealden[10] (21 samples analysed).										
Maximum . .	381·10	·485	·196	·160	6·722	6·735	82·50	35·8	44·7	80·5
Minimum . .	10·52	·014	·006	0	0	·012	2·10	0	3·8	3·8
From chalk[11] (33 samples analysed).										
Maximum . .	159·16	·772	·340	1·700	6·345	7·779	28·50	39·7	47·1	71·5
Minimum . .	32·48	·014	·007	0	·613	·628	1·79	12·0	5·6	23·6
From gravel on the London Clay[12] (49 samples analysed, 37 from London itself).										
Maximum . .	396·50	1·006	·604	2·750	25·840	25·927	34·60	49·2	164·3	191·0
Minimum . .	31·80	·040	·012	0	0	·013	1·90	0	5·7	14·3
From Bagshot beds[13] (8 samples analysed).										
Maximum . .	286·80	1·295	·154	·630	17·940	—	31·15	21·5	111·9	131·7
Minimum . .	23·18	·078	·027	·001	0	·087	2·48	5·4	5·6	13·1
From fluvio-marine series[14] (13 samples analysed).										
Maximum . .	66·12	·429	·093	·016	3·640	3·734	7·20	12·1	29·3	36·4
Minimum . .	8·16	·063	·010	0	0	·010	2·40	0	4·6	4·6
From alluvium and gravel[15] (29 samples analysed).										
Maximum . .	320·72	·931	·940	3·050	11·265	14·300	36·25	36·4	118·6	152·4
Minimum . .	28·58	·015	·010	0	0	·074	1·70	2·7	1·9	4·6

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[1] In almost all cases clear and palatable.

[2] Generally clear and palatable.

[3] Almost all clear and palatable.

[4] In many cases clear and palatable; but in others turbid, and even very turbid.

[5] All clear or slightly turbid and palatable.

[6] Generally clear, or only slightly turbid and palatable. In a few cases saline taste.

[7] Even this water was clear and palatable.

[8] In nearly all cases clear, or slightly turbid and palatable.

[9] Varying from clear and palatable to very turbid. In some cases saline taste.

[10] Mostly more or less turbid. Palatable.

[11] Clear to very turbid. Palatable, or occasionally slight saline taste.

[12] Generally more or less turbid and palatable. Occasionally slight saline taste.

[13] Generally more or less turbid and palatable.

[14] More or less turbid and palatable.

[15] Generally clear or only slightly turbid and palatable. Occasionally slight saline taste.

known as 'Artesian' (from Artois, in France, where they were probably first employed); that is to say, on reaching the water-bearing stratum with the bore-hole the water rises to the level or even considerably above the level of the ground, the phenomenon being due to the underground water being confined under pressure beneath an impervious stratum of clay or the like, and through the outcrop of the water-bearing stratum being at a considerably higher altitude than the point at which the boring has been made. Thus, in the London basin, 'Artesian wells' are obtained by sinking through the London clay into the chalk beneath, which has its outcrop at considerable altitudes in the chalk hills on the north and south of the Thames valley. Owing to the large amount of pumping which now goes on from such water-bearing strata, however, the water of many wells which formerly rose to the surface has now to be pumped. In the great majority of deep wells the water does not rise nearly to the surface, and the pumps have often to be placed at considerable depths in the shaft. It is usual, and highly desirable, to line these wells to a considerable depth with closely-fitting iron cylinders, in order to exclude surface water, and unless this is carefully done the deep wells may become as objectionable and dangerous as shallow ones.

The following tables, in which the same classification as for the shallow wells above is preserved, afford a survey of the general character of these deep well waters obtained in Great Britain. In nearly all the samples of which the maximum, minimum, and average results are given below, it may be taken that the wells were unpolluted by surface water, but for the sake of comparison there are appended to most of the sections analyses of deep well waters from the same strata in which pollution by surface or imperfectly-filtered water is highly probable.

These results most conclusively demonstrate the great superiority from a chemical point of view of the subterranean waters obtained at great depths to those derived from shallow wells. Indeed, these deep well waters are, as regards organic matter, amongst the purest to be found in nature, and hence, unless extremely hard, they are of the best quality for drinking purposes.

Closely associated with these deep well waters is the next group of spring waters.

Deep Well Waters. (6th Rep. Riv. Com. p. 89.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Devonian rocks.										
Maximum. . .	45·30	·083	·016	·001	·696	·713	4·20	26·2	16·4	32·5
Minimum. . .	8·94	·021	·005	0	·044	·049	1·40	·5	3·1	3·6
Average (5 samples)	29·41	·047	·012	0	·400	·412	2·96	8·9	9·4	18·3
Polluted well at Bromyard[1] . .	85·12	·177	·048	0	2·279	2·327	11·25	25·0	16·2	41·2
Polluted well at Dundee[1] . .	27·50	·119	·027	·025	·532	·580	3·05	9·6	8·5	18·1
From millstone grit.										
Well at Bradford, Yorks[1] . . .	55·40	·150	·005	·028	·038	·066	3·23	6·8	7·3	14·1
Well at Glossop, Derby[1] . . .	26·32	·092	·020	·003	·019	·042	·89	9·8	5·9	15·7
From coal measures.										
Maximum . .	144·88	·198	·064	·170	1·468	1·494	59·85	28·2	48·5	75·0
Minimum . .	33·42	·045	·014	0	0	·029	1·29	5·7	1·2	9·9
Average (9 samples)	83·10	·119	·034	·044	·207	·278	18·05	15·1	20·6	35·7
Polluted well at Holyrood, Edinburgh . . .	92·54	·326	·175	·056	·950	1·171	7·95	27·9	8·3	36·2
From magnesian limestone.										
Mansfield, Woodhouse[2] . . .	54·32	·139	·039	0	1·188	1·227	3·20	23·4	26·0	49·4
Pontefract, Yorks[2] .	84·92	·054	·021	0	2·673	2·694	5·55	26·5	40·8	67·3
Sunderland, Durham[2]	44·18	·035	·030	0	·416	·446	4·17	·8	13·9	14·7
From New Red Sandstone.										
Maximum . .	62·84	·091	·038	·039	3·508	3·528	7·51	19·4	20·0	35·6
Minimum . .	14·20	0	0	0	0	·009	1·30	0	4·9	5·7
Average (28 samples)	30·63	·036	·014	·003	·717	·734	2·94	7·4	10·5	17·9

[1] Only two samples analysed.

[2] Only three samples analysed.

Deep Well Waters (continued).

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From New Red Sandstone (continued).										
Polluted well at Lichfield . . .	32·06	·163	·038	·003	·489	·529	2·20	9·3	9·0	18·3
Polluted well at Liverpool . .	86·70	·135	·038	·005	8·678	8·721	12·61	11·5	24·0	35·5
Polluted well at Oxton . . .	27·80	·249	·034	·001	·376	·411	3·52	5·6	8·5	14·1
From Lias.										
Well at Northampton	57·76	·168	·024	·003	0	·026	5·15	8·6	1·7	10·3
Well at Somerton, Somerset . .	84·20	·124	·030	0	·778	·808	3·70	35·3	14·7	50·0
Polluted well at Trowbridge, Wilts .	144·34	·236	·057	·002	·550	·609	36·70	27·4	29·7	57·1
From Oolites.										
Maximum . .	41·90	·054	·018	·110	1·898	1·907	3·70	18·0	10·6	23·0
Minimum . .	26·60	·023	·005	0	0	·099	1·35	8·3	3·6	18·9
Average (5 samples)	33·60	·037	·010	·022	·625	·654	2·69	13·8	6·8	20·6
Polluted maximum of 3 wells . . .	71·04	·217	·053	·002	·778	·800	7·80	26·4	12·9	39·3
Polluted minimum of 3 wells . . .	27·48	·106	·020	0	0	·047	2·10	12·6	8·6	21·2
From Hastings sand, Lower and Upper Greensand, and Wealden.										
Maximum . .	79·20	·120	·021	·074	1·074	1·085	10·00	27·8	26·0	44·3
Minimum . .	28·24	·028	·003	0	0	·007	1·60	1·1	1·2	3·6
Average (20 samples)	45·20	·068	·014	·016	·196	·223	5·38	16·8	10·5	27·3
Polluted well in Lower Greensand at Sevenoaks .	38·76	·447	·072	0	·252	·324	5·90	7·2	13·4	20·6
From chalk.										
Maximum . .	66·34	·131	·064	·029	2·277	2·319	11·10	38·6	13·8	50·0
Minimum . .	23·30	0	0	0	trace	·014	1·00	10·8	2·7	19·1
Average (66 samples)	36·88	·050	·017	·001	·610	·628	2·76	21·2	6·5	27·7
Polluted wells, maximum . . .	216·40	·821	·186	·150	3·401	3·484	106·0	36·1	34·3	51·5
Polluted wells, minimum . . .	32·16	·107	·028	0	0	·204	1·83	13·9	5·3	23·9
From chalk beneath London clay.										
Maximum . .	106·70	·195	·067	·118	·645	·681	38·80	29·5	25·4	48·5
Minimum . .	33·38	·055	·005	0	0	·053	2·38	0	·9	·9
Average (13 samples)	78·09	·093	·028	·048	·068	·135	15·02	9·7	8·7	18·4
Polluted wells at Colchester . . .	96·20	·174	·030	·021	2·582	2·629	21·00	12·7	13·0	25·7
Polluted wells at Hounslow . .	82·40	·273	·042	·001	·846	·889	9·05	26·2	8·1	34·3
From Thanet sand and drift.										
Maximum . .	61·10	·133	·021	·190	·438	·457	9·10	23·7	12·0	34·0
Minimum . .	45·96	·074	·019	0	0	·019	5·20	4·5	3·6	8·1
Average (4 samples)	53·84	·113	·020	·072	·116	·202	6·32	14·4	7·6	22·0

6. *Spring water.* In the following table the results of a large number of, presumably unpolluted, British spring waters are arranged according to the geological nature of the ground from which they are derived, whilst for the sake of comparison the composition of probably polluted spring waters from the same geological sources are in many cases appended.

Spring water. (6th Rep. Riv. Com. p. 107.)

(Result of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From granite and gneiss.										
Maximum	9·44	·119	·019	·002	·204	·210	3·10	1·2	5·3	5·6
Minimum	1·40	0	0	0	0	·013	·55	0	1·2	1·2
Average (8 samples)	5·94	·042	·008	·001	·106	·115	1·69	·4	2·6	3·0
From Silurian rocks.										
Maximum	27·10	·096	·042	·005	·659	·674	3·70	6·9	9·3	15·8
Minimum	3·04	·011	·002	0	0	·011	·90	0	1·5	1·5
Average (15 samples)	12·33	·051	·014	·001	·178	·192	1·84	1·5	5·3	6·8
From Devonian and Old Red Sandstone.										
Maximum	66·90	·124	·034	·006	4·104	4·128	13·80	22·4	12·4	29·9
Minimum	5·50	·009	·001	0	·013	·028	1·30	0	1·9	2·2
Average (22 samples)	25·06	·054	·012	·001	·764	·777	3·85	4·8	7·2	12·0
From mountain limestone.										
Maximum	98·50[1]	·286	·023	·006	1·022	1·036	32·00[1]	20·9	29·5	48·5[1]
Minimum	15·70	·011	0	0	0	·001	·70	2·1	3·3	11·0
Average (13 samples)	32·06	·087	·010	·001	·224	·235	4·63	10·9	8·9	19·8
From Yoredale and millstone grits.										
Maximum	40·80	·109	·028	·006	·617	·650	3·45	21·4	11·5	26·4
Minimum	3·32	·017	·004	0	0	·005	·95	0	2·7	2·7
Average (8 samples)	17·73	·042	·011	·001	·169	·181	1·73	6·6	5·7	12·3
From coal measures.										
Maximum	39·60	·120	·027	·008	1·813	1·860	3·35	14·5	17·1	25·7
Minimum	6·84	·029	·004	0	0	·010	·95	0	2·3	2·6
Average (22 samples from millstone grit and coal measures)	21·91	·050	·014	·001	·393	·408	1·85	5·2	7·9	13·1
From magnesian limestone.										
Pontefract, Yorks	66·52	·058	·038	·002	1·686	1·726	3·40	4·9	34·8	59·7
From New Red Sandstone.										
Maximum	74·26	·118	·069	·014	1·256	1·275	7·00	19·8	25·0	35·7
Minimum	12·90	·027	0	0	0	·006	1·30	0	4·2	8·0
Average (15 samples)	28·69	·065	·017	·001	·330	·349	2·19	8·1	10·7	18·8
From Lias.										
Maximum	58·12	·131	·036	·009	1·332	1·353	4·80	32·3	17·4	45·7
Minimum	21·22	·024	·006	0	0	·035	1·35	9·1	5·3	15·1
Average (7 samples)	36·41	·073	·019	·001	·467	·487	2·48	21·3	8·8	30·1
From Oolites.										
Maximum	52·16	·140	·021	·014	1·157	1·168	3·30	30·0	13·5	38·7
Minimum	22·30	·009	·003	0	0	·014	·97	11·3	3·5	16·9
Average (35 samples)	30·33	·043	·011	·001	·402	·414	1·55	18·2	6·2	24·4
From Lower Greensand, Hastings sand, and Upper Greensand.										
Maximum	68·40	·135	·028	·003	1·116	1·129	7·10	25·0	22·1	40·2
Minimum	4·55	·002	·002	0	·034	·045	1·10	0	·7	·7
Average (19 samples)	30·05	·053	·012	0	·326	·338	2·98	13·6	6·6	20·2
From chalk.										
Maximum	39·30	·097	·023	·006	·863	·874	7·40	25·3	8·1	32·2
Minimum	25·36	·008	·003	0	0	·009	1·05	6·8	3·6	12·4
Average (30 samples)	29·84	·044	·010	·001	·382	·392	2·45	18·1	5·5	23·6
From fluvio-marine, red crag, drift, and gravel.										
Maximum	225·24	·164	·043	·007	1·277	1·293	4·27	32·2	94·3	126·5
Minimum	24·62	·004	·006	0	·004	·034	2·10	·7	6·1	12·6
Average (10 samples)	61·32	·086	·019	·001	·354	·374	2·76	18·0	19·6	37·6

[1] Water supply of Weston-super-Mare; these exceptionally high results doubtless due to access of sea water.

7. *Mineral spring waters.* Many spring waters possess marked medicinal properties in consequence of the materials they hold in solution, but in some cases these properties must be of an imaginary character, as some of the waters in question are only remarkable for their great purity, and have no claim to the title of 'mineral water,' which should be limited to such as contain either exceptional ingredients or ordinary ingredients in unusually large proportions. An immense number of such waters are in use, and have been submitted to careful analysis; a very extensive collection of such analyses is to be found in Raspe's 'Heilquellen Analysen,' Dresden, 1885.

These mineral waters are conveniently classified by Hermann Weber (Quain's Dictionary of Medicine), according to the ingredients which characterise them, into — (1) Simple thermal waters; (2) common salt or muriated saline waters; (3) alkaline waters; (4) sulphated saline waters; (5) iron or chalybeate waters; (6) sulphur waters; (7) earthy and calcareous waters.

(1) *The simple thermal waters,* whilst containing only a moderate proportion of dissolved solids, are characterised by a high temperature, from 27°–65°C., and sometimes by the presence of an unusually large proportion of nitrogen. The principal springs of this class are: Panticosa, Leukerbad, Bormio, Gastein, Pfäffers, Johannisbad, Ragatz, Wildbad, Plombières, Buxton, Bath, Lucca, Teplitz, Schlangenbad, &c.

(2) *Common salt or muriated saline waters* contain sodium chloride as the principal constituent, although this also occurs often in large quantity in many of the other classes of mineral waters. These salt waters or brines are very common in almost all countries. Some of the principal ones in England are: Droitwich, Nantwich, Middlewich, Woodhall, and Harrogate; Leamington and Cheltenham along with sodium sulphate. In Germany: Kissingen, Homburg, Nauheim, Kreuznach, Soden, Pyrmont, Wiesbaden, Ischl, Kreuth, Baden-Baden, &c. In France: Bourbonne-les-Bains, Lamotte-les-Bains, Balaruc, Salins. In Italy: Castellamare, Ischia, Monte Catini, La Porretta. In Switzerland: Bex.

(3) *Alkaline waters* are characterised by the presence of carbonate of soda, almost always with more or less free carbonic acid, and sometimes with a large quantity also of sodium chloride. Of the simply alkaline waters, there are—(*a*) *Hot*: Vichy, Neuenahr, Mont-Dore, Chaudesaigues, Néris; (*b*) *Cold*: Apollinaris, Vals, Salzbrunn, Bilin, Wilhelmsquelle, Taunus, Marcolo; whilst the chief muriated alkaline waters are: (*a*) *Hot*: Ems, Royat, La Bourboule; and (*b*) *Cold*: Luhatschowitz, Selters, Gleichenberg, Rosbach, Vic-sur-Cère. Several of these, but especially La Bourboule and Mont-Dore, contain a marked proportion of arsenic.

(4) *Sulphated waters* contain either sodium or magnesium sulphate, or both, as the prominent ingredients, in some cases also associated with sodium carbonate and chloride. They are often called '*bitter waters.*' The chief simple sulphated waters are: Galthof, Pullna, Saidschutz, Sedlitz, Birmensdorf, Ivanda, Hunyadi Janos, Epsom, Aranjuez, Friedrichshall, Mergentheim; the two latter are also rich in chlorides. Weaker springs of the same kind are found at Leamington, Cheltenham, Scarborough, and at Purton Spa. Of alkaline sulphated waters there are: Carlsbad, Marienbad, Tarasp-Schuls, Franzensbad, Elster, and Bertrich.

(5) *Iron or chalybeate waters* are those in which an unusual proportion of this element is present, either in otherwise comparatively pure water or associated with other mineral matters. Thus, of comparatively pure chalybeate waters, there are those of Schwalbach, Spa, Brückenau, Schandau, Liebwerda, Flinsberg, Freienwalde, Recoaro, Königswarth, Liebenstein, Altwasser, Alexisbad, Muskau, Tunbridge Wells, and one of the springs at Harrogate; whilst of waters in which the iron is associated with a considerable quantity of other salts, there are those of Aratapak, Orezza, Pyrmont, Driburg, Rippoldsau, Griesbach, Antogost, Petersthal, Bocklet, St. Moritz, Reinerz, Godesberg, Cudowa, Imnan, and Santa Catarina.

(6) *Sulphur waters* are those containing appreciable quantities of either sulphuretted hydrogen or the sulphides of sodium, potassium, calcium, or magnesium. Some of the more important thermal sulphur waters are those of Eaux Chaudes, Cauterets, Saint Sauveur, Barèges, Bagnères-de-Luchon, Ax, Escaldes, Le Vernet, Amélie-les-Bains, Uriage, Allevard, Aix-les-Bains, Aix-la-Chapelle, Baden (Austria), Baden (Switzerland), Lavey, Schinznach, Battaglia and Abano in the Euganean Mountains, Panticosa, Mehadia, Helouan, near Cairo; whilst of cold sulphur springs there are those of Eilsen, Neundorf, Langenbrücken, Weilbach, Meinberg, Reutlingen, Enghien, Challes, Stachelberg, Heustrich, Gurnigel, some of the Harrogate[1] springs, Llandrindod, Builth, Moffat, Strathpeffer, Lisdunvarna.

(7) *Earthy and calcareous waters* are characterised by the presence of large proportions of the carbonate and sulphate of lime, and carbonate of magnesia. Some of the more important are found at Wildungen, Lippspringe, Weissenburg, Contrexéville, Bagnères-de-Bigorre, St. Arnaud, Crausac, whilst the table waters of Couzan, St. Galmier, and Taunus are of the same character. (See tables, pp. 952–959.)

8. *Sea water.* The ocean is a great evaporating-basin, which is constantly receiving waters, more or less impure, in the shape of rivers, whilst at the same time it is constantly losing pure water in the form of vapour, the impurities remaining behind and imparting to the sea its well-known saline character, which also distinguishes all lakes which are devoid of outlet, like the Dead Sea, Caspian, Aral, Great Salt Lake, Utah, &c., in which the same process of concentration by evaporation is going on. As will be seen from the accompanying analytical table, the composition of the ocean varies considerably in different places and at different depths, whilst land-locked seas, like the Mediterranean, Black Sea, and Baltic, present even still greater differences.

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[1] For an interesting account of the mineral waters of Yorkshire, in which the composition of the Harrogate springs is traced from 1783 to the present time, see Thorpe, C. J. 1881, 497–516. The 'Chloride of Iron Spa,' Harrogate, is shown to contain ·506–·550 part, the 'Montpellier Strong Sulphur Well,' Harrogate, ·8774 part, and the 'Boston Spa,' Thorp-Arch, ·111 part of barium respectively in 10,000 parts of water.

(Results of Analysis expressed in parts per 1,000.)

Seas	Point of collection of sample	Na	Cl	Mg	Ca	K	SO_4	Br	CO_3	Fe	Fixed Residue	Authors
Atlantic Ocean .	0°47′S.—33°20′W. .	11·081	19·460	0·9568	0·4567	0·7604	2·577	0·4069	—	—	35·700	Bibra, A. u. Pharm. 77, 90.
,,	20°54′N.—40°44′ W. .	10·464	19·012	1·2735	0·4684	0·7252	2·446	0·3102	—	—	34·700	
,,	41°18′N.—36°28′W. .	11·719	20·840	1·1981	0·5568	0·6682	3·029	0·3878	—	—	38·400	
,,	Cape Horn . .	10·457	18·841	1·1763	0·5289	0·5916	2·878	0·3271	—	—	34·800	
North Sea .	. . . .	10·117	18·954	1·3141	0·4782	0·6811	2·563	0·2924	—	—	34·400	
,,	Between Belgium and England . . .	10·206	18·168	1·1582	0·3244	0·3536	2·590	(?)	—	—	32·800	Bischof, C. Géolog., 1, 99.
Straits of Dover	Some miles from Havre . .	10·142	17·794	1·2305	0·4093	0·0425	2·882	0·1046	0·078	traces	32·700	Figuier et Mialhe, J. Ph. [3] 13, 406.
Mediterranean .	Marseilles . . .	10·688	21·099	3·0037	0·048	0·0041	5·716	(?)	0·142	—	40·700	Laurent, J. Ph. 21, 93.
,,	At 3,500 metres from the coast of Cette .	11·706	20·527	1·3104	0·4411	0·2643	2·943	0·434	0·0679	0·0028	37·700	Usiglio, A. Ch. 27, 92, 172.
,,	The Lagunes of Venice	8·779	15·882	1·1646	0·1769	0·4356	2·662	(?)	—	—	29·100	Calamai, 1847.
Pacific Ocean .	3·5 metres below the surface . . .	10·262	18·950	1·3151	0·4719	0·6038	2·786	0·3102	—	—	34·700	Bibra, *l.c.*
,,	140 metres below the surface . . .	10·233	19·321	1·4714	0·4752	0·6336	2·827	0·2394	—	—	35·200	
Baltic . .	. . . .	5·894	10·386	1·6115	0·0363	—	0·719	—	—	—	17·710	Pfaff, Schweigger's Journ. 22, 271.
Black Sea . .	Coast south of the Crimea . . .	5·512	9·574	0·6622	0·1305	0·0975	1·2505	0·005	0·2475	0·1271	17·605	Göbel, P. Suppl., 1, 187.
Sea of Azof .	Between Kertch and Mariapol . .	3·997	6·585	0·4010	0·0908	0·0670	0·8045	0·004	0·0695	0·0358	11·900	*Ibid.*
Caspian Sea .	South west of Pischnoï	1·144	2·737	0·4098	0·1916	0·1397	1·337	(?)	0·0773	0·0401	6·296	*Ibid.*
Dead Sea . .	From the surface .	0·885	17·628	4·177	2·150	0·474	0·2424	0·167	traces	traces	27·078	Terreil, C. R. 62, 1329. (Wurtz, Dictionnaire de Chimie.)
,,	From 300 metres below the surface .	14·300	174·985	41·428	17·269	4·386	0·6276	7·093	traces	traces	278·135	

To these may be added the following analysis of the water of the Irish Channel in the winter of 1870 (Thorpe and Morton, S. C. I. 1871, 506).

(Results of Analysis expressed in parts per 1,000.)

NaCl . . .	26·43918	$MgSO_4$ . . .	2·06608	$CaSO_4$ . . .	1·33158	NH_4Cl . . .	·00044
KCl . . .	·74619	$MgCO_3$ . . .	Trace	$CaCO_3$ . . .	·04754	$FeCO_3$ . . .	·00503
$MgCl_2$ . . .	3·15083	$Mg(NO_3)_2$ . . .	·00207	LiCl . . .	Trace	SiO_2 . . .	Trace
$MgBr_2$ . . .	·07052						

Sp.gr. at 0°C. = 1·02721
,, ,, 15°C. = 1·02184
Total = 33·85946

—	I.—Thermal				II.—Muriated saline
Place	Gastein	Wildbad, Württemberg	Buxton, Derbyshire	Bath	Kissingen, Bavaria
Name of spring	—	Eberhards-brunnen	St. Ann's Well	King's Spring	Bitter Water
Analyst	Ullik, 1864	Fehling, 1859	Muspratt	Merck and Galloway, 1848	Liebig, 1858
Sodium iodide	—	—	—	—	—
,, bromide	—	—	—	—	12·75
Sulphuretted hydrogen	—	—	—	—	—
Sodium sulphide	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Potassium chloride	—	—	—	—	—
Ammonium ,,	—	—	—	—	·29
Sodium ,,	4·28	23·54	3·43	40·61	1280·12
Lithium ,,	·27	—	—	—	1·25
Magnesium ,,	—	—	2·40	2·47	—
Calcium ,,	—	—	—	—	—
Strontium ,,	—	—	—	—	—
Barium ,,	—	—	—	—	—
Aluminium ,,	—	—	—	—	—
Hydrochloric acid	—	—	—	—	—
Iron, metallic	—	—	—	—	—
Potassium sulphate	1·35	1·41	·43	6·62	19·83
Sodium ,,	20·72	3·80	—	—	8·19
Magnesium ,,	·11	—	·11	23·86	1093·29
Calcium ,,	—	—	—	113·49	50·49
Strontium ,,	—	—	—	—	—
Barium ,,	—	—	—	—	—
Ferrous ,,	—	—	—	—	—
Manganous ,,	—	—	—	—	—
Sulphuric acid	—	—	—	—	—
Sodium bicarbonate	—	15·44	—	—	—
Magnesium ,,	·14	1·57	5·67	—	—
Calcium ,,	2·81	13·84	20·34	18·94	91·23
Ferrous ,,	·07	·05	·15	2·10	—
Manganous ,,	—	—	—	—	—
Sodium nitrate	—	—	—	—	—
,, borate	—	—	—	—	—
,, phosphate	·09	—	—	—	—
,, arseniate	—	—	—	—	—
Silica	4·96	6·25	1·49	4·25	—
Sodium silicate	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Lime	—	—	—	—	—
Alumina	·03	·06	—	—	—
Carbonic anhydride	—	—	—	—	—
Oxygen	—	—	—	—	—
Water	—	—	—	—	—
Organic matter	—	—	·50	—	—
	34·83	65·96	34·52	212·34	2557·44

N.B.—The results are expressed

II.—Muriated saline (continued)							III.—Alkaline
Homburg, essen-Nassau	Salzungen, Sachsen-Meiningen	Salzungen	Baden-Baden	Bourbonne-les-Bains	Monte Catini	Castellamare di Stabia	Vichy
Elisabeth-brunnen	Trinkquelle	Saturated Brine	Hauptquelle	Bainromain	Tintorini	Sorgente Muraglione	Mean of 17 springs
Fresenius, 1863	Hofmann	Wöhler	Bunsen, 1871	Mialhe and Figuier, 1849	Casanti, 1863	—	—
·003	—	—	—	—	—	—	—
·32	3·50	3·80	—	6·40	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
34·63	8·60	34·40	15·43	—	—	—	—
2·19	—	—	·50	—	—	—	—
985·79	1187·90	25648·00	214·78	577·10	1189·99	485·08	51·36
2·16	—	—	—	—	—	—	—
76·27	26·10	315·20	1·70	38·10	34·82	12·74	—
65·05	125·10			—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	46·20	1·34	12·90	21·70	—	28·94
—	—	—	—	—	—	—	5·43
—	—	—	—	—	19·58	52·51	—
1·68	31·50	438·60	19·38	87·90	187·71	—	—
1·78	—	—	—	—	—	—	·41
·10	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	499·00
—	—	—	—	—	—	5·14	37·06
222·54	31·80	16·10	17·87	14·10	57·74	100·83	58·35
3·20	·40	1·00	·48	—	—	—	1·66
·21	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
·10	—	—	·29	—	—	—	5·08
—	—	—	—	—	—	—	·24
2·63	—	·70	11·90	—	·70	19·20	5·15
—	—	—	—	12·00	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	·11	2·90	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
1398·653	1414·90	26504·00	283·78	751·40	1512·24	675·50	692·68

in parts per 10,000 by weight.

—	III.—Alkaline (continued)				
Place	Mont-Dore	Chaudes-aigues	Heppingen, Prussia	Bilin, Bohemia	Salzbrunn, Silesia
Name of spring	St. Bertrand	Flegère	Apollinaris	Josephsquelle	Oberbrunnen
Analyst	Lefort, 1862	Chevalier	Bischof, Kyll, and Mohr	Huppert, 1875	Fresenius, 1882
Sodium iodide	—	—	—	—	·0005
Sodium bromide	—	—	—	—	·078
Sulphuretted hydrogen	—	—	—	—	—
Sodium sulphide	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Potassium chloride	—	—	—	—	—
Ammonium ,,	—	—	—	—	·05
Sodium ,,	36·85	14·39	37·65	36·43	16·32
Lithium ,,	—	—	—	1·25	·94
Magnesium ,,	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Strontium ,,	—	—	—	—	—
Barium ,,	—	—	—	—	—
Aluminium ,,	—	—	—	—	—
Hydrochloric acid	—	—	—	—	—
Iron, metallic	—	—	—	—	—
Potassium sulphate	2·96	—	—	23·50	5·28
Sodium ,,	5·18	—	21·28	71·92	45·61
Magnesium ,,	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Strontium ,,	—	—	—	—	·42
Barium ,,	—	—	—	—	—
Ferrous ,,	—	—	—	-	—
Manganous ,,	—	—	—	—	—
Sulphuric acid	—	—	—	—	—
Sodium bicarbonate	56·18	86·07	135·21	478·12	217·29
Magnesium ,,	17·57	2·15	57·52	26·15	47·40
Calcium ,,	34·23	6·77	37·55	59·11	43·83
Ferrous ,,	2·07	1·20	1·67	·38	·57
Manganous ,,	—	—	—	·15	·086
Sodium nitrate	—	—	—	—	·60
,, borate	—	—	—	—	—
,, phosphate	—	—	—	·03	·006
,, arseniate	·09	—	—	—	—
Silica	16·54	9·93	1·37	4·34	3·07
Sodium silicate	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Lime	—	—	—	—	—
Alumina	1·12	—	—	·01	—
Carbonic anhydride	—	—	—	—	—
Oxygen	—	—	—	—	—
Water	—	—	—	—	—
Organic matter	—	·60	—	—	—
Sodium fluoride	—	—	—	—	—
Strontium bicarbonate	—	—	—	—	—
Barium ,,	—	—	—	—	—
	172·79	121·11	292·25	701·39	381·5505

N.B.—The results are expressed

III.—Alkaline (continued)					IV.—Sulphated		
Ems, russia	Royat, Puy-de-Dôme	La Bourboule, Puy-de-Dôme	Luhat-schowitz	Nieder-Selters, Nassau	Sedlitz, Bohemia	Hunyadi Janos	Friedrichshall
ürsten-runnen	St. Victor	Choussy and Perriere	Johannes-quelle	—	—	No. 12	Bitter-water
esenius, 1871	Truchot, 1878	Lefort and Bonis	Ferstl, 1853	Fresenius, 1863	Steinmann	Fresenius, 1878	Liebig, 1847
·002	—	—	2·22	·003	—	—	—
·035	—	—	·97	·091	—		12·76
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	55·33	—	27·90	2·00	—	—	—
·18	—	—	—	·52	—	—	—
00·47	121·52	296·90	362·83	232·22	27·22	142·41	1280·79
·32	3·50	—	·23	·36	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
4·85	20·30	18·98	—	4·35	91·94	13·29	19·82
1·46	—	5·37	—	—	330·40	1966·21	7·53
—	—	—	—	—	1691·33	1949·42	1094·70
—	—	—	—	—	79·36	13·79	50·49
·24	—	—	—	·27	·24	—	—
·10	—	—	—	·02	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
04·72	162·10	195·00	836·66	125·18	—	—	—
20·56	64·64	4·32	10·94	30·81	—	—	—
21·70	101·21	19·01	91·40	44·38	166·27	125·37	91·22
·19	5·60	·42	1·70	·42	—	·28	—
·018	—	—	·57	·07	—	—	—
—	—	—	—	·61	—	—	—
—	—	—	—	—	—	—	—
·165	—	—	·55	·08	—	—	—
—	—	1·94	—	—	—	—	—
4·99	9·50	12·00	5·40	2·12	—	1·12	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
·005	—	—	·17	·018	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	1·04	—	—
—	—	—	·10	—	—	—	—
—	—	—	1·32	—	—	—	—
—	—	—	·80	—	—	—	—
60·005	543·70	553·94	1343·76	443·522	2387·80	4211·89	2557·31

in parts per 10,000 by weight.

—	IV.—Sulphated (continued)				
Place	Leamington	Cheltenham	Scarborough	Carlsbad, Bohemia	Tarasp-Sch Switzerla
Name of spring	Old Well	Montpellier, No. 7	South Wells	Felsenquelle	Ursus-que
Analyst	Brown, 1862	Abel and Rowney, 1848	Thompson	Ludwig, 1879	Hasemann 1875
Sodium iodide	—	·67	—	—	·03
,, bromide	—	4·91	—	—	1·96
Sulphuretted hydrogen	—	—	—	—	—
Sodium sulphide	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Potassium chloride	—	—	—	—	—
Ammonium ,,	—	—	—	—	4·11
Sodium ,,	671·19	857·26	36·23	101·31	284·24
Lithium ,,	—	—	—	1·33	·63
Magnesium ,,	101·67	—	5·51	—	—
Calcium ,,	—	—	—	—	—
Strontium ,,	—	—	—	—	—
Barium ,,	—	—	—	—	—
Aluminium ,,	—	—	—	—	—
Hydrochloric acid	—	—	—	—	—
Iron, metallic	—	—	—	—	—
Potassium sulphate	—	—	—	18·03	27·72
Sodium ,,	—	115·04	—	237·82	167·08
Magnesium ,,	30·20	17·51	32·01	—	—
Calcium ,,	348·19	—	210·17	—	—
Strontium ,,	—	—	—	·037	·03
Barium ,,	—	—	—	—	—
Ferrous ,,	—	—	—	—	—
Manganous ,,	—	—	—	—	—
Sulphuric acid	—	—	—	—	—
Sodium bicarbonate	—	—	—	183·92	344·03
Magnesium ,,	—	14·81	—	24·61	88·11
Calcium ,,	—	35·09	20·51	47·52	241·96
Ferrous ,,	—	—	—	·36	1·75
Manganous ,,	—	—	—	·028	·03
Sodium nitrate	—	—	—	—	·08
,, borate	—	—	—	·36	24·17
,, phosphate	—	—	—	·074	·08
,, arseniate	—	—	—	—	—
Silica	—	3·92	—	7·07	1·03
Sodium silicate	—	—	—	—	—
Calcium ,,	—	—	—	—	—
Lime	—	—	—	—	—
Alumina	—	—	—	·03	·0
Carbonic anhydride	—	—	—	—	—
Oxygen	—	—	—	—	—
Water	—	—	—	—	—
Organic matter	—	26·27	—	Sodium fluoride ·60	—
	1151·25	1075·48	304·46	623·099	1187·0

N.B.—The results are expressed

V.—Chalybeate

walbach, sen-Nassau	Spa, Belgium	Brückenau, Bavaria	Recoara, Italy	Tunbridge Wells	Harrogate	Driburg, Westphalia	Rippoldsau, Baden
hlbrunnen	Sauvenière	Stahlquelle-brunnen	Vigiliana	—	Iron-spring	Haupttrink-quelle	Wenzels-quelle
resenius, 1855	Commission of 1874	Scherer, 1854	Pisanello, 1862	Powell, 1856	Hofmann, 1854	Fresenius, 1865	Bunsen, 1871
—	—	—	—	—	—	—	—
—	—	—	—	—	—		—
·012	—	—	—	—	—	—	
—	—	—	—	—	—	—	
—	—	—	—	—	—	—	—
—	·18	—	—	—	16·11		
—	—	—	—	—	—	·19	—
·67	·69	·83	—	4·22	929·60	7·36	8·46
—	—	—	—	—	—	·035	—
—	—	·42	—	·50	116·84	—	—
—	—	—	—	·66	157·66		
—	—	—	—	—	—	—	—
—	—	—	—	—			
—	—	—	—	—	—		
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
·37	·54	1·90	—	—	—	2·22	4·64
·79	—	—	—	—	—	36·11	95·59
—	—	7·02	21·72	—	—	59·85	32·00
—	—	—	42·77	2·41	—	96·90	—
—	—	—	—	—	—	·47	—
—	—	—	—		—	·01	—
—	—	—	171·76	—	—		—
—	—	—	—	—	—		—
—	—	—	60·90	—	—	—	—
2·06	6·67	—	—	—	—	—	—
21·22	6·82	2·01		—	—	—	4·99
22·13	12·66	22·83		—	100·80	152·44	151·52
8·38	7·72	1·20		8·48	5·45	7·44	12·29
1·84	·16	·48	—	—	—	·43	·30
—	—	—	—	—	—	·05	—
—	—	—	—	—	—	—	—
—	—	·05	—	—	—	·057	—
—	—	—	Ferric sulphate, 192·32	—	—	—	—
3·21	1·09	1·38	—	—	1·34	2·93	9·73
—	—	—	Aluminium sulphate, 35·78	—	—	—	—
—	—	—	Copper sulphate, 3·32	—	—	—	—
—	—	—		—	—	—	—
—	·46	—		·75	—	·01	1·73
—	—	—	—	—	—	—	—
—		—	—	—	—	—	—
—	—	—	—	—	—		—
—	—	6·36	—	—	—	—	—
	36·99	44·48	528·57	17·02	1327·80	366·502	321·25

in parts per 10,000 by weight.

—	VI.—Sulphur				
Place	Eaux Chaudes, Pyrenees	Cauterets, Pyrenees	Aix-les-Bains	Aix-la-Chapelle	Schinzna Switzerla
Name of spring	Source Baudot	Source de César	Sulphur spring	Kaiser-quelle	Sulphu spring
Analyst	Filhol, 1852	Filhol and Reveil	Bonjean, 1838	Liebig-Monheim, 1851	Grandea 1865
Sodium iodide	—	—	—	·05	—
,, bromide	—	—	—	·36	—
Sulphuretted hydrogen . .	—	—	4·14	—	5·5
Sodium sulphide	·87	2·27	—	1·36	·8
Calcium ,, ...	—	—	—	—	—
Potassium chloride . . .	—	—	—	—	—
Ammonium ,, ...	—	—	—	—	—
Sodium ,, ...	11·50	1·78	2·90	261·16	57·2
Lithium ,, ...	—	—	—	·33	—
Magnesium ,, ...	—	—	—	—	6·5
Calcium ,, ...	—	—	—	—	—
Strontium ,, ...	—	—	—	—	—
Barium ,, ...	—	—	—	—	—
Aluminium ,, ...	—	—	—	—	—
Hydrochloric acid . . .	—	—	—	—	—
Iron, metallic	—	—	—	—	—
Potassium sulphate . . .	—	—	—	15·27	10·0
Sodium ,, ...	8·89	·79	6·62	28·34	—
Magnesium ,, ...	—	·008	9·38	—	8·8
Calcium ,, ...	5·81	—	9·42	—	91·1
Strontium ,, ...	—	—	—	·025	—
Barium ,, ...	—	—	—	—	—
Ferrous ,, ...	—	—	—	—	—
Manganous ,, ...	—	—	—	—	—
Sulphuric acid	—	—	—	—	—
Sodium bicarbonate . . .	—	—	—	91·86	—
Magnesium ,, ...	—	—	—	7·71	—
Calcium ,, ...	5·36	—	18·39	22·74	56·5
Ferrous ,, ...	—	—	1·23	1·31	1·3
Manganous ,, ...	—	—	—	—	—
Sodium nitrate	—	—	—	—	—
,, borate	—	—	—	—	—
,, phosphate . . .	—	—	·33	—	—
,, arseniate . . .	—	—	—	—	—
Silica	·26	—	·50	6·61	1·1
Sodium silicate	—	6·57	—	—	—
Calcium ,, ...	—	4·51	—	—	—
Lime	—	Sodium thiosulphate ·20	—	—	—
Alumina	—	—	1·75	—	1·0
Carbonic anhydride . . .	—	Ferrous sulphide ·004	—	—	—
Oxygen	—	—	—	—	—
Water	—	—	—	—	—
Organic matter	—	4·50	1·20	7·69	—
	32·69	20·632	55·86	444·815	240·

N.B.—The results are expressed

VI.—Sulphur (continued)					VII.—Earthy and calcareous		
ngenbrücken, Baden	Heustrich, Switzerland	Harrogate, Yorkshire	Harrogate	Strathpeffer, Scotland	Wildungen	Bagnères de Bigorre, France	St. Galmier, France
aldquelle or Ostringer	Trinkquelle	Montpellier, strong sulphur spring	Weak sulphur spring	—	Helenenquelle	Petit Prieur	Source martiale
unsen, 1861	Müller, 1865	Hofmann, 1854	Hofmann, 1854	Thomson	Fresenius, 1860	Gonderax and Rosière	Bonis, 1864
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
·99	1·69	—	—	16·73	—	—	—
—	3·39	20·38	4·84	—	—	—	—
·98	—	—	—	—	—	—	—
—	—	8·12	—	—	—	—	—
—	—	—	—	—	·57	—	—
1·07	·54	1135·43	330·98	35·33	103·75	8·50	20·00
—	·28	—	—	—	—	—	—
—	—	77·29	28·08	—	—	29·20	—
—	—	87·53	—	—	—	—	—
	—	—	—	—		—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—		—	—	—	—	—
3·66	·64	—	6·61	—	2·78	—	—
16·98	20·05	—	—	96·81	1·35	—	8·00
75·39	—	—	2·06	8·92	—	38·75	—
6·44	—	·84	9·72	56·36	—	163·10	—
—	—	—	—	—	—	—	—
—	—	—	—	—	·058	—	—
—	—	—	—	—	—	—	—
—	—	—		—	—	—	—
—	—				—	—	—
—	67·30	—	—	—	85·38	—	62·12
—	·76	—	—	—	136·38	—	81·68
62·87	1·54	49·23	49·90	—	126·99	58·10	102·24
·83	—	—	—	—	1·87	—	5·93
—	—	—	—	—	·12	—	—
—		—		—	—	—	—
—	—	—	—	—	—	—	—
2·28	·21	—	—	—	—	—	—
—	—	—	—	—	—	—	—
1·73	·90	2·61	·24	—	3·10	5·40	4·50
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	Sodium thiosulphate 2·62	—	—	—	—	—	—
·41	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	1·00	—
173·63	99·92	1381·43	432·43	214·15	462·348	304·05	284·47

in parts per 10,000 by weight.

Thus in the vicinity of the poles the proportion of salt is less than near the equator; similarly, land-locked seas, such as the Black Sea and Baltic, which receive large rivers are less salt; whilst the Mediterranean in most places is more salt than the great oceans. Of salt lakes, the Dead Sea is far more, and the Caspian far less, salt than the oceans. In addition to chloride of sodium, the principal substances present in sea water are the sulphates and carbonates of lime and magnesia, and salts of potassium, whilst in very minute quantities there are found also a number of others, amongst which may be mentioned bromides, iodides, and fluorides, silicic, phosphoric, and nitric acids, iron, silver, copper, lead, arsenic, zinc, cobalt, nickel, lithium, rubidium, and cæsium (Forchhammer, Phil. Trans. 155, 203; Voelcker, Chem. Gaz. 8, 346; Malaguti, Durocher and Sarzeau, A. Ch. [3] 28, 122; Daubrée, C. R. 27, 827; Field, Chem. Gaz. 1857, 93; Hunter, C. J. 8, 16, 144).

For analyses of the waters of the Baltic, Red Sea, and especially of the Dead Sea *v.* J. 1866, 985–987.

The volume of gas dissolved in sea water is, according to Hunter (C. J. 1870, 20), very small —only from 2·2–3·5 vols. of gas in 100 vols. of water. The

	CO_2 Per cent.	O Per cent.	N Per cent.
2·2 vols. consisted of .	28·62	49·44	21·94
3·5 „ „ .	48·28	17·22	34·50

(*V.* Jacobsen, D. P. J. 1877, 223, 330).

A very extensive investigation of the composition of sea water was made in connection with the voyage of H.M.S. *Challenger*, and the elaborate report prepared thereon by Dittmar (Report on the Composition of Ocean Water, 1884) should be consulted for detailed information on this subject. From 77 complete analyses, the following numbers for the average composition of ocean-water salts are calculated:

Average composition of ocean-water salts, in parts per 100 *of total salts* (Dittmar).

Chlorine	55·292
Bromine	·1884
Sulphuric acid (SO_3)	6·410
Carbonic acid (CO_2)	·152
Lime (CaO)	1·676
Magnesia (MgO)	6·209
Potash (K_2O)	1·332
Soda (Na_2O)	41·234
(Basic oxygen equivalent to the halogens)	.(−12·493)
	100·000

As regards the salinity of the ocean, this was found to vary, expressed in parts of total salts per 1,000 parts of sea water, between the following limits: Minimum (from the southern part of the Indian Ocean, south of 66° lat.), 33·01; maximum (from the middle of the North Atlantic, at about 23° lat.), 37·37.

As regards the carbonic acid in sea water, Dittmar comes to the following conclusions: (1) Free carbonic acid in sea water is the exception; as a rule, the carbonic acid is less than the proportion corresponding to bicarbonate. (2) In surface waters the proportion of carbonic acid increases when the temperature falls, and *vice versâ*. (3) Within equal ranges of temperature it seems to be lower in the surface water of the Pacific than it is in the surface water of the Atlantic Ocean.

For the bacteriology of sea water (the number of micro-organisms in sea water at a distance from land is very small) see p. 992.

Drinking water. It is in its capacity as a beverage that water is of most general importance and interest, and more and more attention is annually given to the careful selection of water for this purpose. As has long been known, the palate is by no means a safe guide in such choice, for although unpalatable waters are obviously unsuitable for drinking, palatable waters may contain materials capable of doing most serious injury. The guidance of the palate leads to waters which are highly impregnated either with organic or inorganic ingredients being discarded; but as almost infinitesimally small proportions of certain forms of organic matter are capable of producing the most serious effects, it follows that the negative indications of taste require supplementing. It is now established beyond question that the diseases known as 'zymotic' are due to minute forms of life known as micro-organisms, and in a number of cases the specific forms responsible for such diseases have been discovered, identified, and carefully studied (*v.* FERMENTATION). Of zymotic diseases there are only two—Asiatic Cholera, and Typhoid Fever—which are with certainty known to be frequently propagated by drinking water, and in the case of these two diseases authorities are almost fully agreed as to the particular organisms to which they are due (*v. Examination of drinking water*). The propagation unquestionably takes place through the excreta of persons suffering from these diseases gaining access to water which is afterwards used for drinking, whilst water contaminated with the sewage of healthy persons is generally believed to be capable of producing diarrhœa and other minor disturbances in those drinking it.[1]

It is thus obvious that the presence of even minute quantities of sewage matters in drinking water must be viewed with the gravest suspicion, whilst much larger proportions of vegetable matter may be regarded as harmless; indeed, waters containing much vegetable matter (which may give rise to diarrhœa) will generally be avoided in consequence of their unpalatability and generally brown colour. In selecting water for drinking purposes it is necessary, therefore, in the first instance, to make a careful inquiry as to the possibility of the water having been in contact with refuse animal matters, and if possible all waters open to such suspicion should be discarded. For the same reason it is of the first importance in the examination of water to

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[1] It has, indeed, been recently asserted (Arloing, Internat. Congress of Hygiene, London, 1891) that a bacillus, bacillus coli communis, which is normally present in healthy fæces, may become converted, under suitable conditions, into the true exciting cause of typhoid; such a metamorphosis would serve to explain the sudden appearance of typhoid in places where no infection from a previous typhoid patient can be traced. The assertion cannot be regarded, however, as adequately proved.

Upland Surface Water Supplies.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			Remarks
								Temporary	Permanent	Total	
The Vyrnwy, June 14, 1867	3·73	·218	·005	·003	·011	·018	·74	·3	1·1	1·4	Clear and colourless. (Future supply to Liverpool.)
Thirlmere Lake, May 13, 1867	2·66	·194	·004	·003	·002	·008	·52	0	·7	·7	Clear and colourless. (Future supply to Manchester.)
Loch Katrine Water, Nov. 16, 1891	2·80	·149	·025	0	·004	·029	·72	—	—	·6	Slightly turbid. (Glasgow water supply.)
Bolton water supply (Entwistle reservoir)	9·37	·297	·018	·024	·010	·048	1·19	·1	5·0	5·1	Slightly turbid.
Manchester water supply, May 9, 1874	7·00	·132	·031	·003	0	·033	·90	0	2·7	2·7	Turbid.
Leeds water supply, Sep. 29, 1869	15·00	·258	·025	0	0	·025	1·30	1·8	6·5	8·3	Clear.
Bradford water supply, Oct. 6, 1869	10·10	·582	·079	·004	0	·082	1·02	·9	5·5	6·4	Very turbid. (High level service.)
,, ,, ,, ,,	13·20	·396	·036	·003	·026	·064	1·13	·8	6·3	7·1	Turbid. (Low level service.)
Sheffield water supply, Dec. 20, 1872	8·36	·356	·057	·001	·032	·090	·85	0	4·4	4·4	Turbid.
Edinburgh water from Crawley Burn, Sep. 22, 1868	11·28	·187	·031	·001	0	·032	1·04	·7	5·4	6·1	Clear.
Newcastle water supply, Sep. 16, 1868	23·40	·237	·062	0	0	·062	1·59	5·8	8·1	13·9	Clear.
Durham water supply, Oct. 5, 1870	54·50	·082	·020	0	·041	·061	4·85	11·6	13·4	25·0	Slightly turbid.
Kilmarnock water supply, April 7, 1870	12·44	·508	·032	0	·028	·060	1·40	1·0	7·6	8·6	Clear.
Chester water supply, May 19, 1873	16·84	·219	·043	0	0	·043	2·00	5·0	5·7	10·7	Turbid.
Wakefield water supply, April 15, 1892	6·20	·075	·010	0·36	Traces	·040	1·05	·8	2·2	3·0	Turbid.
Carlisle water supply, Sep. 23, 1868	13·10	·233	·037	·001	0	·038	·99	3·5	5·2	8·7	
Gloucester water supply, March 18, 1870	24·82	·375	·042	0	·026	·068	1·52	16·0	3·6	19·6	Turbid.
Preston water supply, July 31, 1868	12·44	·236	·031	·006	0	·036	1·59	3·7	5·3	9·0	Slightly turbid.
Darwen water supply, Dec. 1887	7·80	·158	·028	·002	0	·030	1·10	0	3·5	3·5	(High level service.)
,, ,, ,, ,, ,,	13·40	·248	·030	·004	·065	·041	1·10	0	7·1	7·1	(Low level service.)

discover what evidence, if any, there is of the water having been in contact with such refuse substances. In the present state of our knowledge this is a very difficult matter, as, although the results of a careful chemical analysis frequently point to such contamination when on a sufficiently large scale, on the other hand it is generally impossible to prove the negative; nor does the bacteriological examination, so useful in many other respects, help us materially in this case. It becomes, therefore, of the greater importance to make a thorough inspection of the source and to trace out the further history of the water, a matter which is too frequently neglected in practice, for unless this be done the results of the scientific examination may often receive an erroneous interpretation. As, however, it is comparatively rarely that natural waters are to be met with which are absolutely above suspicion of *any* contamination with refuse animal matters, it is generally necessary to be satisfied with relative purity, and thus the examination, chemical and biological, of drinking waters becomes a matter of the very highest importance and utility. The natural waters which can lay claim to the greatest degree of safety for drinking purposes are of two distinct kinds.

1. Unpolluted surface waters (generally upland waters).
2. Naturally filtered waters (spring and deep well waters).

In the first case the waters, both by inspection and analysis, must bear no evidence of animal contamination, and this is generally only possible in the case of waters which are found at altitudes above that of human habitations. A number of our large towns are supplied with water of this kind, although the gathering-grounds do in most cases contain some houses, so that absolute freedom from sewage contamination cannot generally be guaranteed. In the table on p. 961 the chemical composition of some of these upland surface water supplies is recorded.

The majority of these upland surface waters are either very soft or of only very moderate hardness, and as in many of these towns extensive manufactures are carried on, these supplies are not only valued because of their safety for drinking, but also on account of their fitness for industrial purposes. It should always be remembered, however, that these surface waters may at times receive more or less sewage contamination, and that the ova of animal parasites derived from the cattle grazing on the gathering-grounds may also be present, and that, therefore, to reduce these sources of danger to a minimum, it is highly desirable that such waters should be carefully filtered through sand before delivery. This is, unfortunately, only done in comparatively few cases.

In the second class of water its original purity is a matter of secondary consequence, the guarantee of safety resting upon the exhaustive process of filtration which the water has undergone in passing through porous strata of the earth's crust. This filtration effects, on the one hand, the more or less complete chemical purification of the water from organic substances, and on the other hand the mechanical removal of organised matters, such as bacteria and animal parasites. The most perfectly-filtered waters of this kind are those obtained from springs and from deep wells, and, again, many of our towns are supplied with water of this kind—more especially from the chalk, greensand, Oolite, and New Red Sandstone formations, which constitute vast filter beds of marvellous efficiency. In the table on page 963 is recorded the chemical composition of the water supplied to some of our towns from such sources.

Of other forms of drinking water we have river waters and shallow-well waters, upon both of which a very large portion of the population is dependent for domestic supply. Both of these classes of water are open to grave objections, and nearly all the best-authenticated cases of the propagation of cholera and typhoid through drinking water have been those in which the latter was obtained from shallow wells. It will be readily understood that the danger in the case of both these classes of water lies in the facility with which sewage matters can gain access to them, rivers passing, as they do, through populated districts and receiving directly or indirectly the drainage of the entire basin, whilst shallow wells are generally sunk in the immediate vicinity of human habitations, where the soil is frequently saturated with animal refuse, the latter often finding its way into these wells without meeting with any formidable obstacle. Indeed, until the information gained upon recent bacteriological research was to hand, it was only surprising that the mischief caused by these classes of water was not more frequent. We now know (*v. Bacteriology of water*) that there are many potent influences tending to remove bacteria from water which, on *a priori* reasoning, would have been regarded as almost, if not wholly, inoperative. These causes are mainly the process of precipitation going on in the flow of a river, and the resistance offered by even a comparatively small thickness of soil or other porous material to the passage of micro-organisms. But although these causes are to be looked upon as highly fortunate, and tending to keep the evils which can result from contaminated drinking water within narrower limits than might have been anticipated, still the possibility of their failure must be constantly kept in view, and they must not for a moment be allowed to check the endeavour to substitute unimpeachable for suspicious sources of supply, which endeavour has been one of the most conspicuous features of both ancient and modern sanitary reform.

Where such suspicious sources of supply are actually in use it becomes, of course, of the highest importance to bring all the resources of modern science to bear upon the question. Every effort must be made to exclude all avoidable sources of contamination, to select the best water only which the source affords, and to submit the latter to the most effective purification which is available. The improvements which can thus be brought about in water supplies obtained from suspicious sources is most conspicuously exemplified in the case of the London supply derived from the rivers Thames and Lea. Here, on the one hand, increasing vigilance has been exercised by the Thames and Lea Conservancy Boards in the exclusion of dangerous

Water Supplies from Deep Wells and Springs.

(Results of Analysis expressed in parts per 100,000.)

Description of water supply	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			Remarks
								Temporary	Permanent	Total	
Deep wells.											
Accrington, from coal-pit, June 11, 1869	33·42	·045	·017	0	·012	·029	1·40	7·7	2·2	9·9	Clear.
Sunderland (magnesian limestone), Sep. 16, 1868	44·18	·035	·030	0	·416	·446	4·17	·8	13·9	14·7	Clear.
Nottingham (New Red Sandstone), March 1, 1869	26·04	·027	·007	·002	·817	·826	1·50	14·9	11·3	26·2	Clear.
St. Helens ,, May 23, 1868	21·66	0	0	0	·436	·436	1·94	5·9	6·8	12·7	Clear.
Northampton (Lias), May 11, 1868	57·76	·168	·024	·003	0	·026	5·15	8·6	1·7	10·3	Clear.
Scarborough (Oolite), Dec. 9, 1873	41·90	·054	·011	0	·539	·550	3·40	12·1	9·1	21·2	Clear.
Eastbourne (greensand), Feb. 22, 1873	43·12	·058	·010	·004	·130	·143	10·00	13·8	7·1	20·9	Slightly turbid.
Folkestone ,, August 9, 1873	41·14	·091	·021	·004	0	·024	4·20	24·6	7·0	31·6	Clear.
Brighton (chalk), Jan. 18, 1873	30·24	·018	·009	0	·644	·653	3·10	14·8	6·4	21·2	Clear.
Bury St. Edmunds (chalk), Nov. 17, 1871	39·00	·089	·020	0	·481	·501	2·15	22·6	7·4	30·0	Clear.
Dover (chalk), March 1, 1873	29·60	·034	·008	·001	·452	·461	2·60	18·6	5·0	23·6	Clear.
Hull (chalk), Jan. 11, 1873	31·66	·032	·012	0	·406	·418	1·95	21·3	4·7	26·0	Clear.
Ipswich (chalk), Nov. 30, 1874	48·60	·064	·017	·002	·943	·962	3·90	23·7	12·3	36·0	Clear.
London (Kent Company's water), (chalk), April 20, 1891	38·80	·069	·016	0	·329	·345	2·30	22·1	7·1	29·2	Clear.
Braintree (chalk below London clay), April 3, 1873	106·70	·068	·033	·094	0	·110	38·80	8·7	5·0	13·7	Clear.
Springs.											
Plymouth (granite and gneiss), June 10, 1871	3·50	·050	·019	0	0	·019	1·30	0	2·1	2·1	Turbid.
Melrose (Silurian), April 5, 1870	14·50	·013	·002	0	·077	·079	1·32	4·5	6·2	10·7	Clear.
Jedburgh (Old Red Sandstone), March 31, 1870	21·94	·021	·003	0	·124	·127	1·30	12·7	6·9	19·6	Clear.
Totnes (mountain limestone), Sept. 30, 1872	22·14	·019	·003	0	·245	·248	2·05	8·1	9·1	17·2	Clear.
Cheltenham (New Red Sandstone), May 31, 1873	21·22	·123	·036	0	·305	·341	1·35	9·1	6·0	15·1	Slightly turbid.

matters from the rivers and their tributaries, whilst on the other hand the water companies have removed their intakes to points on these streams above the most serious pollutions, by increasing their storage capacity they are enabled to avoid drawing from the rivers in times of flood, and by improving their filtering appliances they secure a more perfect purification of the water which they have abstracted. By these combined exertions the water supplied to London to-day is both chemically and hygienically a very different thing from what it was forty years ago, although still derived from the same streams, which in the ordinary course of events would be more polluted now than they were then.

Importance to be attributed to various ingredients of drinking water. It is only possible here to give a very brief account of the importance which is usually attributed to the several ingredients which are commonly determined in the analysis of drinking waters.

Dissolved gases. The gases present in ordinary drinking waters are those of the atmosphere—oxygen, nitrogen, and carbonic anhydride. Their quantitative determination is rarely made, as they are of little or no significance in connection with the quality of the water for drinking, excepting that through the absence of dissolved gases a water has the flat taste of that which has been recently boiled. It is sometimes supposed that the absence of a due proportion of dissolved oxygen in water is an indication of the presence of decomposing organic substances, but this can only be the case with surface waters, as the very purest subterranean waters are almost entirely destitute of it. In the following table the proportion of the several dissolved gases in different kinds of water is recorded :—

Gases dissolved in 100 cubic inches of water	Rain-water	Cumberland mountain water	Loch Katrine water	Thames water	Deep chalk well water
	cubic inches	cubic inches	cubic inches	cubic inches	cubic inches
Nitrogen	1·308	1·424	1·731	1·325	1·944
Oxygen	·637	·726	·704	·588	·028
Carbonic acid	·128	·281	·113	4·021	5·520
	2·073	2·431	2·548	5·934	7·492

The large proportion of dissolved carbonic anhydride in the Thames and deep chalk well water is mainly combined with calcium carbonate as bicarbonate.

Total solid residue. It is only rarely that the amount of the residue left by a water on evaporation affords any evidence of its fitness for drinking. As a general rule, it may be stated that waters which contain very small residues are probably pure and unpolluted, but on the other hand many waters of the highest organic purity contain large proportions of mineral matter in solution (*v.* analysis of spring and deep well waters). It is impossible to assign any limits to the proportion of mineral matter which may be present in water without interfering with its fitness for drinking, more especially as opinion is very divided as to the influence of the several constituents of this mineral matter on health. Thus it has been contended that the presence of lime and magnesia salts in drinking water is very desirable as affording the necessary elements for bone-formation, whilst by others the presence of these materials is regarded as of no consequence, whilst others again view their presence in more than very moderate proportions as liable to give rise to calculus and other concretions ; whilst the continuous use of a magnesian water is often supposed to be productive of goitre and cretinism (*v. Hardness of water*). Suffice it to say here that nearly all the best drinking waters in the United Kingdom yield less than 50 parts of solid residue per 100,000, and most of them very considerably less (*v.* analyses above). The use of waters yielding much larger residues is generally excluded on other than hygienic grounds, viz. the great inconvenience which attends the employment of such waters for general domestic purposes, in consequence of their unfitness for boilers and washing.

Organic matter. As will be pointed out (under *Water analysis*), the accurate determination of the organic matter in water is attended with insurmountable difficulties, and none of the methods of analysis in use claim to effect more than a partial determination, or to throw indirect light upon its amount. Thus in the 'combustion process' the organic carbon and nitrogen are determined with more or less accuracy, in the alkaline permanganate process that portion of the organic nitrogen is discovered which is readily convertible into ammonia, whilst in the 'permanganate' or 'oxygen' process the proportion of permanganate destroyed by the organic matter is taken into account. Although it may be generally stated that the smaller the proportion of organic matter the more desirable is the water for drinking, still of greater importance is the determination of the origin of the organic matter present, whether animal or vegetable. As already pointed out, the presence of vegetable matter is of comparatively little consequence, more especially as even small amounts interfere with the palatability of the water, what is known as a 'peaty taste' being imparted by any amount yielding much in excess of ·2 part per 100,000 of organic carbon. Sometimes much light may be thrown on the origin of the organic matter in water by the proportion which the carbon and nitrogen exhibit towards each other, especially when this is considered in connection with the proportions of ammonia, nitrates, nitrites, and chlorine. Inasmuch as animal in general contains a much higher proportion of nitrogen to carbon than does vegetable matter, it follows that the higher the ratio of nitrogen to carbon in the organic matter present in a sample of water, the more probability is there, *cæteris paribus*, of its being derived from animal sources and *vice versâ*. The possibility of such diagnosis, however, is considerably limited through the observed fact that in the oxidation of peaty matter the organic carbon disappears much more rapidly than the nitrogen; whilst, on the other hand, in the oxidation of animal matter there is conversely a tendency for the organic carbon to become concentrated, thus leading to a simulation of animal matter in the case of vegetable, and a simulation of vegetable matter in the case of animal substances after oxidation. These phenomena are illustrated by the following figures taken from the Sixth Report of the Rivers Pollution Commission, pp. 6–10:—

Proportion of carbon to nitrogen in peat	11·4 : 1
Proportion of organic carbon to organic nitrogen in unoxidised peaty matter contained in upland surface water .	11·9 : 1
Ditto after exposure to atmospheric oxidation in lakes or large reservoirs.	5·9 : 1
Proportion of organic carbon to organic nitrogen in spring water containing peaty matter	3·3 : 1
Proportion of carbon to nitrogen in animal organic matter dissolved in water:—	
Fresh urine	·99 : 1
Average of fresh sewage from sixteen water-closet towns . . .	2·1 : 1
Average of fresh sewage from fifteen midden towns	2·1 : 1
Urine preserved for twenty-four days without oxidation. . . .	1·6 : 1
Proportion of carbon to nitrogen in the animal matter contained in polluted shallow wells . . .	3·1 : 1

Still more misleading is the proportion in the case of sewage which has been submitted to downward filtration through soil. Thus:—

Average of twelve samples of sewage before filtration . . .	C : N = 1·8 : 1
Ditto after filtration through quartz sand	,, = 7·7 : 1
Ditto after filtration through sand and chalk	,, = 6·9 : 1
Ditto after treatment on Beddington sewage-farm	,, = 6·5 : 1

It is thus essential that the evidence afforded by the proportion of organic carbon to nitrogen should be supplemented by an inspection of the source, and by a consideration of the mineral nitrogenous ingredients—ammonia, nitrates, and nitrites—all of which are principally derived from the decomposition of animal matters.

It has often been attempted to classify waters according to the proportions of organic elements which they yield on analysis. Such classifications are, however, fraught with great danger if rigidly applied, and are only here introduced as giving some kind of indication of the quantities ordinarily met with in potable waters:

I. *Upland Surface Water.*

Class I. Water of great organic purity, in which the sum of organic carbon and nitrogen do not exceed ·2 part per 100,000.

Class II. Water of medium purity, in which these elements lie between ·2 and ·4 part.

Class III. Water of doubtful purity, in which they lie between ·4 and ·6.

Class IV. Impure water, in which they exceed ·6 part.

II. *Water other than Upland Surface.*

Class I. Water of great organic purity, in which they do not exceed ·1.

Class II. Water of medium purity, in which they lie between ·1 and ·2.

Class III. Water of doubtful purity, in which they lie between ·2 and ·4.

Class IV. Impure water, in which they exceed ·4.

Albuminoid ammonia. The ammonia yielded on distillation with alkaline permanganate is so frequently made the only measure of the organic matter present in water that a few words are necessary to indicate what is the importance to be attached to the results obtained in this simple process. According to the most recent statements of its author, Mr. Wanklyn, 'deep spring water is often so pure as not to yield ·01 part of albuminoid ammonia per million; and unless mixed with surface water does not yield so much as ·05 part.' 'The filtered water supplied by water companies—no matter whether derived from a lake, from clean mountain streams, or from defiled rivers—yields from ·05 to ·10 parts of albuminoid ammonia per million; and, indeed, if the filtration be efficient, approximates to ·05.' 'When the filters are over-taxed, as happens in the rainy season and in the winter, water companies supply imperfectly-filtered water, in which as much as from ·10 to ·20 part of albuminoid ammonia is found.' This statement must be accepted with great reserve, for in the winter months such surface waters almost invariably contain a much larger proportion of organic matter than during the dry season, thus accounting for the increase in albuminoid ammonia quite irrespective of any over-taxing of the filters. The following figures actually obtained by Mr. Wanklyn will serve to illustrate the kind of results to be expected:

	Parts per million Ammonia	
	Free	Albuminoid
Deep Well Waters.		
Caterham water . .	·04	·00
Cold Harbour, Dorking .	·01	·00
Frome, Somerset . .	·00	·02
Kirby Lonsdale . .	·01	·03
Chatham . . .	·03	·03
Henley-on-Thames . .	·02	·02
Kent Company, London .	·01	·02
Upland Surface Water.		
Manchester water . .	·01	·06
Edinburgh ,, . .	·00	·07
Glasgow ,, . .	·00	·08
London Water.—Filtered River Water.		
West Middlesex Co. (July, 1867)	·01	·07
Grand Junction Co. (July, 1867)	·01	·08
Ditto (Dec. 1867) . .	·00	·16
New River Co. (July 1867)	·01	·05
Chester Water (River Dee)	·00	·07

Contaminated Waters.

	Parts per million Ammonia	
	Free	Albuminoid
Thames above Hampton Court, unfiltered	·04	·28
Thames at London Bridge, high tide	1·02	·59
Pump in Bishopsgate St., London	7·50	·25
Pump in Edinburgh	·21	·29
Well at Eton	·00	·84
Effluent from sewage	16·20	·90

(Water Analysis, J. A. Wanklyn, 1889).

For remarks as to the quantitative value of albuminoid ammonia process, *v.* p. 988.

Oxygen or permanganate process. The analytical value of measuring the proportion of organic matter in water by the amount of permanganate it is capable of decolourising is discussed in the section of this article on *Water analysis*, and it will be sufficient here to give some idea of how the results are to be interpreted. As in the case of the organic elements determined by combustion, it has here again been attempted to establish a scale of classification, which, however, must also be used with the greatest caution and in conjunction with the other analytical data, as well as with regard to the water's source and history. Thus the following artificial standards have been suggested:—

—	Oxygen absorbed in three hours from permanganate of potash by 100,000 parts of water	
	For Upland Surface Water	For other Water
Class I. Water of great organic purity	0–·1 part	0–·05 part
„ II. „ „ medium	·1–·3 „	·05–·15 „
„ III. „ „ doubtful	·3–·4 „	·15–·2 „
„ IV. Impure water	above ·4 „	above ·2 „

It will be readily understood that a great drawback to this permanganate process consists in its not distinguishing between nitrogenous and non-nitrogenous organic matter. Hence it is very desirable that, if the combustion process cannot be resorted to, it should be supplemented by a determination of the 'albuminoid ammonia.'

Mineral nitrogen (ammonia, nitrates, and nitrites). The importance of these ingredients is an entirely indirect one. In themselves they in no way influence the wholesomeness of drinking water; but, on the other hand, they are of the greatest consequence in indicating what the previous history of the water has been. Thus, in the ordinary process of decomposition to which organic matters are subjected in nature, the nitrogen is principally liberated in the form of ammonia, and this, by subsequent fermentative oxidation (*v.* Fermentation and Nitrification), may become converted into nitrites and nitrates. Moreover, owing to the far greater average richness in nitrogen of animal over vegetable matters, it is evident that these primary and secondary products of decomposition furnish the most valuable evidence as to the previous contact of water with nitrogenous, and more especially animal, substances. As a general rule, moreover, the presence of ammonia indicates a more recent contact with such matters than does that of nitrates or nitrites, although in the case of some deep subterranean waters (*v.* analyses of deep well waters from the chalk beneath the London clay) it appears that the nitrates originally present in the water have undergone reduction to ammonia, and hence the latter in such cases must be regarded as evidence of a more remote character even than the nitrates themselves. Again, in the ordinary course of nitrification in nature the ammonia is wholly converted into nitrate, the preliminary oxidation to nitrite being rapidly passed over; but if water containing nitrates is brought in contact with organic matter, these nitrates become more or less reduced to nitrites through the agency of certain micro-organisms (P. F. Frankland, C. J. 1888, 373; Warington, *ibid.* 742), and hence the presence of nitrites generally constitutes evidence of contamination with organic matter subsequent to the original nitrification, rather than to the latter having been imperfect. The fact must also not be lost sight of that nitrates can be reduced by certain microbes in the presence of organic matter with elimination of the nitric nitrogen in the free state, or as oxides of nitrogen, and that a contamination of the nitrified water may thus lead to the more or less complete removal of the mineral nitrogen. The absence of nitrates may thus, under some circumstances, actually indicate contact with animal matter instead of freedom from the same (Munro, C. J. 1886, 632).

It must also be remembered that, in the case of surface waters, the mineral nitrogen may undergo removal through being taken up as food by plant-life present in them, and thus the evidence of previous contact with animal matters be destroyed.

As the hygienic significance of contact with animal matters consists in the possibility of the ingress of pathogenic microbes (which may at any time be present in sewage and similar animal refuse), it is obvious that the evidence of such previous contact which is afforded by the presence of mineral nitrogen in any excessive proportion must be viewed as serious, if the history of the water furnishes no guarantee that any such organised poisons which may have gained access would have been subsequently removed, whilst the evidence is of far less consequence, or may indeed become entirely negligible, if in the subsequent history of the water it has undergone processes of purification which practically preclude the possibility of such poisons being still present. Until the recent application of bacteriology to questions of water supply, it was not possible to ascertain the efficiency of processes of water purification in this respect. But we now know that the exhaustive filtration through porous strata which spring and deep well water has undergone practically guarantees the removal of any micro-organisms which may have been originally present; in the case of river and shallow well waters, on the other hand, the chance of such removal is very much less, and hence in such waters the evidence afforded by mineral nitrogen of previous contact with animal matters must be viewed with great suspicion, whilst in the spring and deep well waters it need excite little alarm, and may often be disregarded altogether (*v.* analyses).

Chlorine. This element is invariably in a state of combination—generally as sodium chloride, and hence quite innocuous. Its determination in potable water, however, is of great importance as often affording valuable information as to whether the water has been in contact with refuse animal matters or not. In this respect it is often more useful than the mineral nitrogen, as, once present in water, it cannot by any natural processes be removed. Its diagnostic value is due to the fact that human urine contains 500 parts of chlorine, or 824 parts of common salt, in 100,000 parts. It is, of course, inapplicable in the vicinity of the sea and of natural salt deposits. In British waters free from animal pollution the average proportion of chlorine may be taken as 1 part per 100,000; but it is subject to very great variations. The following figures will serve to illustrate this point:

Rain-water.

	Chlorine. Parts per 100,000
London (average of samples collected in 1869)	·12
Birkenhead (Liverpool)	·31
Scotland (inland country places)	·33
England (inland country places)	·39
Manchester (average of 1869 and 1870)	·57
Scotch towns (Glasgow not included)	·57
Newcastle-on-Tyne	·79
English towns	·85
Glasgow	·87
St. Helens	·93
Liverpool	·99
Scotland (west coast country places)	1·19
Scotland (east coast country places)	1·26
Runcorn	2·50
Ireland (Valentia)	4·73
England (Land's End)	21·80
India (Ootacamund)	·04

Unpolluted upland surface water.

	Chlorine. Parts per 100,000
Devonshire (10 samples):	
Maximum	2·10
Minimum	1·20
Average	1·53
Midland districts of England (29 samples):	
Maximum	1·52
Minimum	·57
Average	·99
West coast of England (43 samples):	
Maximum	2·00
Minimum	·52
Average	1·12
North-east coast of England (13 samples):	
Maximum	1·59
Minimum	·65
Average	1·04
Western side of Scotland (23 samples):	
Maximum	1·52
Minimum	·70
Average	1·11
Eastern side of Scotland (40 samples):	
Maximum	1·40
Minimum	·35
Average	·84
Rhine at Schaffhausen	·20
Lake Zug (Switzerland)	·27
Lake Zürich (Switzerland)	·17
Sewage from midden towns (20 samples):	
Maximum	21·50
Minimum	6·50
Average	11·54
Sewage from water-closet towns (36 samples):	
Maximum	21·50
Minimum	4·00
Average	10·66
Drainage from fields dressed with farmyard manure and nightsoil (17 samples):	
Maximum	3·35
Minimum	·60
Average	1·54

There are, however, many other refuse liquids besides sewage which contain large quantities of chlorine. Thus the effluents from dye and bleach-works, tanneries, paper-mills, alkali-works, and especially tin-plate and galvanising works, are often very rich in this element, the proportion being often far in excess of anything ever found in sewage (Rivers Pollut. Commiss. 6th Rep. pp. 18–21).

In America recently great attention has been bestowed on the proportion of chlorine present in unpolluted water at different distances from the sea-board. The points at which such waters exhibit the same amount of chlorine are joined by lines termed 'isochlors,' and these isochlors are found to be roughly parallel to the coast-line. Any water submitted for examination is then remanded for further inquiries if it exhibits more chlorine than is normal for the isochlor upon which the source of the particular water is situated. This is an attempt to make the chlorine a measure of the sewage contamination past and present, in much the same way as the proportion of total combined nitrogen has been employed by others. It has the advantage over the latter, inasmuch as the chlorine is practically permanent whilst the nitrogen is removable in various ways; but, on the other hand, the chlorine is subject to great variations within a small area, according to local circumstances, more especially geological. The chlorine, moreover, only testifies to contamination by liquid, and not by solid, excrements, and in this respect also is of less general applicability than the total combined nitrogen. For a description of these 'isochlors,' as well as for a vast amount of careful work on the subject of water supply and sewerage, the reader is referred to 'Examinations by the State Board of Health of the Water Supplies and Inland Waters of Massachusetts, 1887–90.'

Hardness. This term is applied to those ingredients in water which react with soap and produce an insoluble 'curd,' the principal substances in question being the various salts of lime and magnesia, which, entering into double decomposition with sodium stearate (hard soap) or potassium stearate (soft soap), give rise to calcium and magnesium stearates, both of which are insoluble bodies, and soluble salts of sodium or potassium. On this account the salts of lime and magnesia are manifestly detrimental to the fitness of the water for washing, but this will be discussed more in detail under *Water for Industrial Purposes* (*v.* p. 975). As regards the influence of these salts upon the quality of drinking water, opinion is very much divided. Some persons consider the presence of a certain proportion of these salts desirable as furnishing the materials necessary for bone-formation, others contend that if present in more than a moderate proportion they tend to cause calcareous concretions in the system, whilst, lastly, others regard their presence or absence as immaterial from a hygienic point of view. Further, by some authorities the sulphates and chlorides of calcium and magnesium (the so-called 'permanent hardness') are regarded as more objectionable than the bicarbonates or 'temporary hardness.' This was notably the view taken by Edmund Parkes and Allen Miller (Roy. Commis. on Water Supply, 1869, 195, 436). Again, there are many who view the presence of the salts of magnesia with more suspicion than those of lime, and, indeed, magnesian waters are very generally credited with the power of causing phosphatic calculi, goitre, and cretinism. On this account it has sometimes happened that waters which were otherwise of most unimpeachable quality have been discarded in consequence of their containing a few parts per 100,000 of magnesia. All these views concerning the influence of lime and magnesia salts are, however, based upon very unsatisfactory evidence. (For a concise *résumé* of this evidence *v.* Rivers Pollution Commission, 6th Report, 184–201.) The Rivers Pollution Commissioners, in prosecuting their inquiry into this subject, collected the following statistics:—

Hardness of Water	No. of Towns	Average Population	Average Mortality per 1,000
0–5 parts per 100,000 . . .	26	73,366	29·1
5–10 ,, ,, ...	25	81,655	28·3
Above 10 ,, ,, ...	60	44,797	24·3
16–32 ,, ,, ...	London	3,254,260	24·6

As these results are flagrantly illusory, owing to nearly all the large manufacturing towns with conditions notoriously unfavourable to health being supplied with soft water, the Commissioners proceeded to compare towns only of the same class, and in which presumably the other conditions of life would be approximately similar, as follows:—

Description	No. of Towns	Average Population	Average Mortality
Towns supplied with Soft Water.			
Seaport	5	162,801	29·4
Inland Manufacturing	5	172,860	29·7
,, Non-manufacturing . . .	8	10,751	25·4
Watering-places	5	48,430	19·5
Towns supplied with Moderately Hard Water.			
Seaport	3	226,172	32·1
Inland Manufacturing	8	108,715	26·9
,, Non-manufacturing . . .	4	62,372	26·0
Watering-places	3	33,480	19·2
Towns supplied with Hard Water.			
Seaport	6	116,406	25·1
Inland Manufacturing	5	144,981	25·5
,, Non-manufacturing . . .	20	29,169	23·2
Watering-places	12	53,170	20·4

Upon these statistics the Commissioners remark 'where the chief sanitary conditions prevail with tolerable uniformity, the rate of mortality is practically uninfluenced by the softness or hardness of the water supplied to the different towns, and the average rate of mortality in the different water divisions varies far less than the actual mortality in the different towns of the same division. We are, therefore, of opinion that, whilst waters of excessive hardness may be productive of calculus and perhaps other diseases, soft and hard water, if equally free from deleterious organic substances, are equally wholesome.' The question of magnesia in drinking water has been recently discussed by the writer (' What is the Importance of Magnesia in Drinking Water ' P. F. Frankland, Transactions of the Internat. Congress of Hygiene and Demogr., London, 1891), from whose inquiry it appears that whilst the amount of magnesia in the water supplied to most large towns is very small—generally not more than 1–2 parts of MgO per 100,000—it is much larger than is generally supposed in the well-water consumed by such a

Description		Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			Remarks
									Temporary	Permanent	Total	
Spring water from Newark-on-Trent, used for brewing purposes		257·05	·046	·013	0	·465	·478	2·9	17·2	162·8	180·0	
	(II.)	Fe_2O_3 and Al_2O_3		CaO	MgO	Na_2O	SO_3	N_2O_5	SiO_2	—	—	
		·14		82·89	14·74	4·68	131·51	1·79	·98		—	
Pontefract water supply from magnesian limestone	(I.)	88·84	·035	·010	0	3·315	3·325	5·9	16·6	37·2	53·8	Total MgO = 9·23.
Well in bunter beds of New Red Sandstone at Sandiacre, Derbyshire	(I.)	45·04	·097	·037	·021	·094	·148	2·0	19·5	18·7	38·2	Total MgO = 7·05. Total CaO = 10·78.
Spring at Matlock Bath, Derbyshire	(I.)	47·84	·021	·002	0	·030	·032	4·1	18·8	15·3	34·1	Total MgO = 4·08. Total CaO = 11·57.
Bore hole in alluvium near River Derwent, Matlock Bath	(I.)	24·44	·117	·048	·020	0	·064	·9	9·0	8·2	17·2	Total MgO = 2·53. Total CaO = 5·60.
Boring in New Red Sandstone at Gainsborough, Lincolnshire	(I.)	49·97	·028	·008	0	0	·008	2·0	16·8	18·6	35·4	
	(II.)	·19		11·94	5·97	2·84	16·62	0	·94	—	—	
Waters from Malvern: No. 1	(I.)	27·48	·092	·024	0	·668	·692	1·9	11·6	9·6	21·2	Total Magnesia = 1·09.
No. 2	(I.)	8·52	·015	·016	0	·354	·370	1·2	0	4·3	4·3	Ditto = ·75.
No. 3	(I.)	12·56	·033	·014	0	·277	·291	1·5	2·9	5·0	7·9	Ditto = 1·64.
Wells at Wellingborough before softening	(I.)	58·20	·036	·017	·004	0	·020	2·2	30·3	16·2	46·5	
Ditto	(II).	·35		21·97	4·05	2·31	11·30	0	1·01	—	—	
Ditto after softening with lime	(I.)	26·30	0·35	·014	·004	0	·017	2·2	1·1	14·9	16·0	
Ditto	(II.)	·02		6·42	2·16	2·24	12·03	0	·63	—	—	
Well in chalk, Southampton, before softening	(I.)	31·69	·024	·012	·005	·365	·381	1·6	23·0	2·7	25·7	
Ditto	(II.)	·14		11·53	·25	1·21	·39	1·41	1·02	—	—	
Ditto after softening with lime	(I.)	14·07	·021	·013	·004	·381	·397	1·6	5·6	3·0	8·6	
Ditto	(II.)	·11		4·42	·28	1·12	·45	1·47	·94	—	—	
New River Company's water, London, before softening	(I.)	32·08	·150	·018	0	·308	·326	2·1	19·1	3·6	22·7	Total MgO = ·92. Total CaO = 12·35.
Ditto after softening with lime	(I.)	13·48	·103	·017	0	·329	·346	2·1	1·9	3·4	5·3	Total MgO = ·80. Total CaO = 2·14.
Well in chalk below London clay, London	(I.)	59·29	·036	·013	·010	0	·021	8·3	10·0	0	10·0	Alkalinity (calculated as Na_2O) = 8·69.
Ditto	(II.)	·20		3·20	1·97	24·85	11·41	0	1·25	—	—	
Well in chalk below London clay, Victoria Dock, London, before softening	(I.)	58·76	·111	·017	·050	0	·058	16·7	19·8	8·0	27·8	
	(II.)	·22		12·57	2·82	13·13	1·96	0	1·44	K_2O = ·93		
Ditto after softening with lime and caustic soda	(I.)	44·20	·084	·016	·060	0		17·3	2·4	6·0	8·4	
	(II.)	·14		5·96	·57	15·76	4·01	0	·69	K_2O = 1·06		
Deep well in New Red Sandstone at St. Helens	(I.)	56·40	·099	·029	·004	0	·032	3·6	29·4	11·8	41·2	
Ditto	(II.)	·15		15·76	6·31	5·82	7·33	0	·97	K_2O = ·33		
Ditto after softening with lime	(I.)	—	—	—	—	—	—	—	—	—	15·7	
Ditto	(II.)	—	—	4·25	5·41	—	—	—	—	—	—	

NOTE.—The figures standing in a horizontal line commencing with 'I.' refer to 'Total Solid Matters,' 'Organic Carbon,' &c., whilst those in a line commencing with 'II.' refer to 'Fe_2O_3 and Al_2O_3,' 'CaO,' 'MgO,' &c.

(Results of Analysis expressed in parts per 100,000).

large portion of the population. Thus in the case of fifty brewery waters from all parts of the kingdom, the average amount of magnesia (MgO) was 3·41 parts per 100,000. It must also be remembered that the geological formation richest in magnesia (the magnesian limestone) is only very slightly represented in this country, so that the proportions of magnesia met with in the dolomitic districts of the Continent must be much larger. As the recorded analyses in which magnesia has been determined are comparatively few in number, those made by the writer are shown on the previous page.

These analytical results show that the calcareous waters derived from the chalk contain only a very small proportion of magnesia, and that even in the highly-saline waters obtained from the chalk below the London clay the amount is also very moderate, only distinctly greater than in the case of the normal chalk waters.

The proportion of magnesia, again, is considerably greater in the water from the Lias, as represented by the wells at Wellingborough, whilst the largest proportions were found in waters from the magnesian limestone and New Red Sandstone.

It will be further seen that in all cases in which the proportion of magnesia is at all considerable (say, upwards of 4 parts), the permanent hardness is high (10 parts per 100,000 or upwards), whilst in none of the cases quoted is the permanent hardness above 10 without the magnesia being above 4 parts; in fact, in waters with low permanent hardness there is little chance of finding much magnesia, and *vice versâ*. Applying this rule, it will be found that in all probability an immense number of waters in common use must contain from 4–6 parts of magnesia per 100,000—a proportion which by some authorities is regarded as objectionable. Thus, of 28 samples of deep well water from the New Red Sandstone analysed by the Rivers Pollution Commission, no less than 16, or more than 50 p.c., contained upwards of 10 parts of permanent hardness. Again, of 15 spring waters from the New Red Sandstone 7 exhibited upwards of 10 parts of permanent hardness. On the other hand, of 66 deep well waters from the chalk, only 5, or 7·5 p.c., had upwards of 10 parts of permanent hardness; and of 28 spring waters from the chalk there was not one in which the permanent hardness amounted to 10 parts per 100,000.

If this investigation be extended to shallow wells, it will be found that the number of probably magnesian waters becomes enormously greater. Thus, of 87 samples of shallow-well water from the New Red Sandstone, no less than 84, or 96·5 p.c., had their permanent hardness in excess, and generally largely in excess, of 10 parts per 100,000; and again, of 33 samples of shallow well water from the chalk, 27 exceeded the 10 parts of permanent hardness. Thus, without at all forcing the rule as to the relationship between permanent hardness and magnesia, it is obvious that waters containing from 4–6 parts of magnesia must be of very common occurrence indeed, and that a very large portion of our population must be supplied with them. Until, therefore, a far more searching inquiry than hitherto has been made into the alleged effect of such waters upon health, it would appear undesirable that any importance should be attributed to such proportions of magnesia in drinking water which are otherwise of unimpeachable purity.

The effect of Clark's process on magnesian waters is noteworthy. As a general rule, the proportion of magnesia removed by the treatment with lime is small—much smaller than that of the lime removed; but it is particularly worthy of notice that in the case where caustic soda was used in conjunction with lime, as is now frequently done in the softening of water for industrial purposes, the proportion of magnesia removed was greater than that of the lime.

In the following table are recorded the proportions of lime and magnesia in a series of 50 brewery waters analysed by the writer from all parts of the country, although in only a few instances can the precise source of the samples be assigned :—

Brewery waters.

(Parts per 100,000.)

—	Lime combined as carbonate	Total lime	Total magnesia
No.			
1	11·96	18·21	·31
2	7·49	7·74	3·90
3	14·37	17·21	·20
4	1·04	10·69	9·99
5	13·91	20·67	·81
6	3·36	6·26	2·24
7	12·31	15·16	4·36
8	3·24	6·34	1·34
9	12·89	15·44	·76
10	0	25·94	9·01
11	16·27	20·46	1·81
12	12·81	16·47	1·87
13 (from Chapel-en-le-Frith, Derbyshire) .	0	1·04	·57
14 (from Brighton) .	14·06	20·87	1·11
15 (chalk below London clay)	2·81	2·81	1·33
16 (from Cosham, Hants)	17·41	23·46	2·84
17 (from Brighton) .	10·30	13·69	·41
18 Ditto . . .	11·51	16·39	·61
19 (from Wrexham) .	16·99	21·14	2·77
20	6·40	10·74	·89
21	10·37	10·69	6·21
22	5·54	5·54	1·74
23	9·53	11·13	·54
24	13·11	15·67	·19
25	2·84	3·37	1·40
26	14·91	19·94	5·01
27	5·91	7·16	1·07
28 (from Reading) .	15·90	25·57	1·21
29	7·11	14·57	5·50
30	20·26	23·04	8·81
31	8·16	8·16	2·57
32	14·51	17·00	7·36
33 (from Cardiff) . .	5·04	14·86	3·91
34	19·34	28·89	2·14
35 (from Louth) . .	11·60	13·36	1·16
36 (from Taunton) .	9·79	10·16	1·27
37	9·91	9·94	4·14

Average magnesia = 3·41 parts per 100,000.

Brewery waters (continued).

(Parts per 100,000.)

—	Lime combined as carbonate	Total lime	Total magnesia
No.			
38	9·36	11·87	·56
39	13·94	15·21	·39
40	·34	3·73	1·61
41	17·64	32·56	5·99
42	7·16	51·66	27·10
43	12·71	46·60	20·57
44	10·74	19·10	·60
45	10·74	12·29	1·19
46 (from Hertford) .	12·61	14·37	·76
47	·29	4·96	2·59
48	10·04	11·00	3·03
49	3·29	3·39	3·30
50 (chalk below London clay)	—	2·61	1·46

Average magnesia = 3·41 parts per 100,000.

The hardness of water not unfrequently throws light upon its previous history, for the food of both man and animals is of necessity rich in lime, and nearly the whole of this is in adult life again found in the liquid and solid excreta; hence water obtained from strata which have been much polluted with animal matters always exhibits a large amount of permanent hardness (*v.* analyses of shallow well waters). A description of the principal processes in use for the softening of hard water will be found under *Water for industrial purposes* (*v.* p. 975).

Purification of Drinking Water.

Inasmuch as the impurities are either suspended or dissolved, mineral or organic, and the organic either animate or inanimate, it follows that the subject of purification may be considered from a number of different points of view, according to the particular class of impurities the removal of which is under discussion. Again, the processes of purification fall under two heads, according as they are suitable for application on the large or small scale only. Practically all the more important processes of drinking water purification are filtration processes, those depending upon precipitation being more especially of importance in connection with water for industrial purposes (see p. 975).

Purification of drinking water on large scale. All surface water is liable to turbidity, and in times of rain and flood the amount of suspended matter may become very excessive. It is, therefore, highly desirable that all surface water, even that from upland sources, should be submitted to purification before distribution for domestic purposes. The process of purification is much facilitated if the water is first permitted to remain at rest in storage reservoirs for some days or even weeks, the greater part of the suspended matter thus becoming precipitated, and some destruction even of the dissolved organic matter also taking place. The process of filtration resorted to on the large scale is almost invariably that through sand of different degrees of coarseness. This method was inaugurated by Simpson, the engineer to the Chelsea Company in 1829 ('London Water Supply,' Francis Bolton, 1884, p. 164), and has since been adopted by all the other London companies not drawing their supplies from wells, as also in the case of a number of other towns both at home and abroad. The filter beds, as usually constructed, are 10–16 feet in depth, often upwards of an acre in area, made water-tight with masonry, concrete, or puddled-clay walls. On the bottom are collecting drains, upon which is placed a layer of broken stone about two feet in thickness, following upon which are layers of coarse gravel, fine gravel, and uppermost a stratum of fine sand, 1–4 feet in thickness. The water is kept at a depth of 1–4 feet above the surface of the fine sand, the rate of filtration varying in different works. The greater part of the suspended impurities are retained in the downward passage of the water by the first few inches of fine sand, which sooner or later, sometimes in the course of a few weeks, causes the clogging of the filter. When the rate of filtration is too much retarded for practical purposes, the fouled surface of the sand is removed, after which the filtration can be continued until the filter is again choked, when the surface is again scraped off, the process being repeated until the stratum of sand becomes too thin to be efficient, after which a new filter bed has to be prepared. The sand scraped off is generally thoroughly washed, allowed to dry, and then used again. The following particulars for the several London companies will serve to illustrate the method of working:—

Seventeenth Annual Report of Local Government Board, 1887–8, *p.* 157.

Names of companies	No. of days' supply stored in subsiding reservoirs	Filtering area per million gallons of average daily supply	Thickness of sand on filter				Monthly rate of filtration per square foot per hour	
			Maximum		Minimum		Average	Maximum
		Acres	Ft.	in.	Ft.	in.	Gallons	Gallons
Chelsea	14·0	·67	4	6	4	0	1·75	1·75
East London	16·5	·81	2	0	0	8½	1·33	1·33
Grand Junction	4·0	·74	2	0	1	8	1·8	2·2
Lambeth	8·0	·44	3	0	1	9	2·5	2·9
New River	6·0	·57	2	3	1	3	2·08	2·5
Southwark and Vauxhall . . .	3·0	·64	3	0	1	0	1·5	1·5
West Middlesex	8·0	·99	3	3	2	3	1·33	1·75

Besides the filter beds just described, some of the Thames companies are now using an auxiliary process of filtration through the natural gravel beds which form the banks of the Thames at Hampton. These gravel beds are at all times full of water, which forms, as it were, an underground river, and underground pipes were first laid in this gravel and connected with a pumping well in order to utilise this water, which is always clear and bright in consequence of the natural filtration which it has undergone. In order to increase the supply of this underground water the gravel bed is flooded with water directly from the Thames, for which purpose a second series of perforated pipes are laid parallel to the first and placed at a distance of about thirty yards from them. This second series of pipes is placed in direct communication with the Thames, but at the point of ingress is placed a small vertical sand filter to arrest the coarser impurities. In this manner about three million gallons of well filtered water are daily obtained from forty acres of ground ('Collection, Storage, Purification, and Examination of Water,' Chatham Lectures, 1886, Sir F. Bolton and P. F. Frankland). The excellent results thus obtained has led to the extension of the system in connection with the Thames supply to London, as well as in other places.

Such sand filters, although very efficient in removing the suspended matter, have comparatively little action upon that which is dissolved. Thus the following figures exhibit the composition of the York water supply, before and after filtration through sand:—

(Results of Analysis expressed in parts per 100,000.)

—	Before filtration	After filtration
Total solid matters	28·40	26·20
Organic carbon	·123	·119
Organic nitrogen	·025	·022
Ammonia	0	0
Nitrogen as nitrates and nitrites	·077	·089
Chlorine	1·6	1·6
Temporary hardness	11·5	10·9
Permanent hardness	7·1	7·1
Total hardness	18·6	18·0
Micro-organisms (colonies yielded by 1 c.c. of water on cultivation with gelatine-peptone)	31,200	122

(P. F. Frankland, S. C. I. 1887.)

Until quite recently it was supposed that such sand filtration could have little or no effect in removing the micro-organisms present in water, as the interstitial spaces between the grains of sand are so large in comparison with the minute dimensions of the microbes. It was first shown by Koch in Germany, and by the writer in this country, that nearly all the microbes in water are removed by the sand-filters (Koch, 'Bericht der Deputat. f. die Verwaltung der Canalisationswerke,' Berlin, 1883; P. F. Frankland, Pr. 1885; Proc. Inst. Civ. Engineers, 1885–6; S. C. I. 1885, 1887), and this result has been confirmed by numerous other investigators (Wolffhügel, Arbeiten a. d. k. Gesundheitsamte, 1886, 1; Plagge and Proskauer, Zeitsch. f. Hygiene, 2, 1887, 401).

It was, in fact, supposed by Koch and his pupils that the sand filtration really removed *all* the microbes originally present in the water, and that those always found in the filtered water had gained access subsequent to filtration. The writer had, however, from the first shown that in the case of his regular examinations of the London water supply there was an obvious relationship between the number of microbes in the unfiltered and filtered waters respectively, necessitating the conclusion, therefore, that the sand filters can only be credited with removing *a portion and not the whole of the micro-organisms present.* This is sufficiently conspicuous from the tables on next page, which record some of the writer's results obtained with the London water supply during the year 1886, and reported to the Local Government Board (P. F. Frankland, S. C. I. 1886). The unfiltered Thames water was in every case collected near the intakes of the several water companies at Hampton, and the filtered water from the mains of the Chelsea, West Middlesex, Southwark, Grand Junction, and Lambeth Companies respectively.

C. Fraenkel and Piefke (Zeitsch. f. Hygiene, 8, 1890, 1–40) have quite recently demonstrated by direct experiment that particular species of bacteria purposely introduced into the unfiltered, were still present, although in greatly-diminished numbers, in the filtered water.

The wonderful efficiency of these sand filters in removing microbes was at first very difficult to account for, but it is now recognised to depend upon the impervious nature of the slimy deposit which forms upon the surface of the sand, and until such a coating has been established the filter has but little effect in removing micro-organisms (Piefke, 'Aphorismen über Wasserversorgung,' Zeitsch. f. Hygiene, 7, 1889, 115–170). The rate at which filtration is carried on is also a most important factor, the more rapid the rate the less efficient being the purification (P. F. Frankland, Proc. Inst. Civ. Engineers, 1885–6). The statistics of the London water companies show that the cost of filtration as carried out by them averages about 0·6*d.* per 1,000 gallons.

In countries liable to extreme cold—indeed, even in cold winters in this country—the process of sand filtration offers great difficulties, in consequence of the freezing of the filters; and this has, in Berlin, been guarded against by the construction of a number of covered filter-beds. In the United States, where the same difficulty exists, the Hyatt system of filtration has been employed on a considerable scale. In this the water is first treated with a minute quantity of alum (about $\frac{1}{2}$ grain per gallon), after which it passes through a steel filtering chamber, consisting of a vertical cylinder the diameter of which is nearly twice its height. This cylinder is divided by a horizontal diaphragm, capable of withstanding the hydrostatic pressure necessary for rapid filtration. The lower half contains the filtering material, composed of 2 parts coke and 3 parts sand. The upper part of the cylinder is used for washing the filtering material, which at regular intervals is transferred into it in a state

TABLE I. 1886.

Total number of Colonies obtained by cultivation of one cubic centimetre of water.

—	Description of water					
	Thames unfiltered	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	45,400	159	180	2,270	4,894	2,587
February	15,800	305	80	284	208	265
March	11,415	299	175	1,562	379	287
April	12,250	94	47	77	115	209
May	4,800	59	19	29	51	136
June	8,300	60	145	94	17	129
July	3,000	59	45	380	14	155
August	6,100	303	25	60	12	1,415
September	8,400	87	27	49	17	59
October	8,600	34	22	61	77	45
November	56,000	65	47	321	80	108
December	63,000	222	2,000	1,100	1,700	305
Average	20,255	146	234	524	630	475

TABLE II. 1886.

Percentage reduction in the number of developable micro-organisms present in the river waters before delivery by the companies.

—	Description of water				
	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	99·7	99·6	95·0	89·2	94·3
February	98·1	99·5	98·2	98·7	98·3
March	97·4	98·5	86·3	96·7	97·5
April	99·2	99·6	99·4	99·1	98·3
May	98·8	99·6	99·4	98·9	97·2
June	99·3	98·3	98·9	99·8	98·5
July	98 0	98·5	87·3	99·5	94·8
August	95·0	99·6	99·0	99·8	76·8
September	99·0	99·7	99·4	99·8	99·3
October	99·6	99·7	99·3	99·1	99·5
November	99·9	99·9	99·4	99·9	99·8
December	99·7	96·8	98·3	97·3	99·5
Average percentage reduction . .	98·6	99·1	96·7	98·2	96·2

of violent agitation by hydraulic currents, the impurities flowing away through pipes situated near the top of the cylinder. In the process of filtration the water is admitted through pipes to the upper part of the lower section of the cylinder, and it is drawn off through perforated cups, which permit the water, but not the sand, to pass. It is claimed that the efficiency of the system depends more upon the successful precipitation and entanglement of germ life by the coagulant alumina than upon any special merits of the filter ('Potable Water,' Floyd Davis, Iowa, U.S., 1891). The cost of maintenance is said to be only one-fifth of that entailed by filter beds.

Of other methods of drinking-water purification on the large scale the only one that need be mentioned is Anderson's, which has been very successfully employed in dealing with the highly-impure water which is alone available at Antwerp. The method consists in passing the water slowly through revolving iron cylinders about two-thirds filled with iron borings. A small quantity of the iron continuously passes into solution, so that the water becomes impregnated with ferrous iron, which subsequently, when the water flows into a settling-tank, is converted into the ferric state with precipitation, a large proportion of the organic matter in solution being removed in the process, whilst the antiseptic action of the dissolved iron and the precipitation combined effect a very considerable diminution in the number of vital germs. After undergoing oxidation in the settling tank, the water is finally filtered through sand before distribution. At Antwerp it takes three and a-half minutes for the water to pass through the rotating cylinder, the entire process occupying about six hours (Anderson, Proc. Inst. Civ. Engineers; Engineering, 39, 525).

Purification of drinking water on small scale. The filtration of water on the small scale was already known to the ancients. Thus Pliny mentions vessels in which water was clarified by passage through wool. An immense number of different materials have been employed during recent years, but space will only permit of the brief consideration of a few of the more important ones.

Animal charcoal is employed in a number of common household filters, and from the invaluable services which it yields in sugar-refining it was anticipated that it would be highly efficient as a water filter. Unlike sand, it not only acts upon the suspended matters, but also removes a considerable proportion of the dissolved organic matter, and even some of the temporary hardness. Unfortunately, however, its action is very transient, and it generally soon becomes the seat of numerous organic growths, which are favoured by the phosphate of lime it contains, and the filtered water is then often rendered more impure than the unfiltered.

Vegetable charcoal has but little effect on the dissolved organic matters, although if in a sufficiently fine state of division it is an excellent strainer for suspended impurities (see table below).

Bischof's spongy iron, obtained either by reduction of hæmatite or of roasted pyrites, has a remarkable power of removing dissolved organic matters, as well as temporary hardness and nitrates, and this power is far more permanent than that of animal charcoal. It was for some time also employed on the large scale, in conjunction with sand, at the Antwerp Waterworks. The effect of filtration through animal charcoal and spongy iron respectively is exhibited in the table below.

Since the recent great advances in bacteriological science, it has become evident that the removal of micro-organisms from drinking water is a matter of much greater importance than the removal of organic matter, and hence it is in respect of this property that the value of filters is now generally estimated. The writer has shown (The Removal of Micro-Organisms from Water, P. F. Frankland, Pr. 1885) that several substances—such as coke, wood, charcoal, spongy iron, &c.—in a sufficiently fine state of division are capable of entirely removing all microbes in water passed through a stratum of a few inches of these materials. This power, which is quite independent of any chemical action (thus in the case of coke and wood-charcoal there is little or no removal of dissolved organic matter), is, however, not maintained unless the materials are frequently renewed; and in the case of animal charcoal which has been in use for a short time (one month) the number of microbes was found to be far greater in the filtered than in the unfiltered water. The most conspicuous instance of biological, as opposed to chemical, filtration is furnished by Chamberland's unglazed porcelain filter, which entirely removes microbes, but has no chemical action whatever (see table below).

(Results of Analysis, expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			No. of developable micro-organisms in 1 c.c. of Water
								Temporary	Permanent	Total	
London water, unfiltered [1]	24·60	·129	·023	0	·188	·211	1·6	—	—	19·4	—
Ditto, after filtration through fresh animal charcoal [1]	19·40	·029	·007	·013	·194	·212	1·6	—	—	15·2	—
London water, unfiltered [1]	25·94	·164	·030	·002	·062	·094	1·9	—	—	19·7	—
Ditto, after filtration through animal charcoal in use 11 months [1]	25·10	·010	·002	·002	·125	·129	1·9	—	—	19·1	—
London water, unfiltered [1]	25·28	·120	·013	0	·166	·179	1·7	14·5	6·7	21·2	—
Ditto, after filtration through fresh spongy iron [1]	13·70	·025	·004	·002	·031	·037	1·7	7·4	4·6	12·0	—
London water, unfiltered [1]	24·10	·188	·034	·001	·120	·155	1·95	11·8	7·3	19·1	—
Ditto, after filtration through spongy iron in use 8 months [1]	14·84	·089	·020	·001	0	·021	1·95	5·3	4·3	9·6	—
Water, before filtration [2]	24·80	·144	·050	0	·190	·240	1·9	11·3	5·6	16·9	26,000
Ditto, after filtration through fine coke [2]	25·00	·107	·038	0	·202	·240	1·9	11·3	5·6	16·9	0
Ditto, after filtration through fine wood charcoal [2]	24·68	·090	·024	0	·221	·245	1·9	12·5	4·6	17·1	0
London water, before filtration [3]	33·70	·282	·028	0	·288	·316	1·9	15·7	4·9	20·6	54
Ditto, after filtration through Chamberland filter [3]	30·04	·284	·027	0	·289	·316	1·9	14·4	5·3	19·7	0

[1] Riv. Commis. 6th Rep.

[2] P. F. Frankland, S. C. I. 1885.

[3] P. F. Frankland, Pr. 1885, 390.

A number of household filters in actual use have been examined with regard to their power of removing microbes by Plagge (Public Health Section of Germ. Assoc. of Naturalists and Physicians, 1886), who divides them into six classes, according to the materials used: (1) *carbon filters*, (2) *stone and sand filters*, (3) *spongy-iron filters*, (4) *paper filters*, of several kinds, (5) *porous earthenware filters* (Chamberland), (6) *asbestos filters* (Breyer, Hesse, Arnold, and Schirmer). The carbon filters were found not only to admit of the free transmission of microbes, but in some cases the numbers in the filtrate greatly exceeded those in the unfiltered water. Thus in one case 68 colonies were obtained from 1 c.c. of the unfiltered, and 12,000 from 1 c.c. of the filtered water. The stone and sand filters were all found to be worthless. The spongy-iron filter yielded the following results: unfiltered water, 38,000 colonies from 1 c.c.; filtered, 18,000–24,000 colonies from 1 c.c. The paper filters all yielded very unsatisfactory results; the earthenware and asbestos filters, on the other hand, gave in nearly every instance a filtrate practically free from microbes. (For particulars concerning the sterilising power of the Chamberland filter, see also Miquel, Analyse Bactériologique des Eaux, Paris, 1891.) The principal drawback to these porous earthenware filters is the rapid diminution in the rate of filtration which they exhibit. More satisfactory in this respect are said to be the Berkefeld filters, similarly constructed of burnt infusorial earth (Nordtmeyer, Zeitsch. f. Hygiene, x. 1891, 145; Bitter, *ibid.* 155). Neither the Chamberland nor Berkefeld filters permanently yield sterile water, some of the bacteria in the unfiltered water sooner or later growing through the pores. It is, however, doubtful whether any of the ordinary pathogenic bacteria would do this, as none of them are known to actually multiply extensively in ordinary drinking water (Kübler, Zeitsch. f. Hygiene, viii. 1890, 48).

Purification of drinking water by distillation. This is, of course, the most effectual mode of freeing water from all its impurities. It is resorted to, on a considerable scale, at sea, both for steam and sailing vessels. (For description of forms of apparatus in actual use *v.* Fischer, Technologie d. Wassers, Brunswick, 1880, 201–208.) The insipid taste of the distilled water can be removed either by aëration, or by filtration through animal charcoal or other porous substances. Distilled water is also employed to some extent for the manufacture of aërated waters and for artificial ice.

Purification of drinking water by ebullition. The purification consists, of course, only in the destruction of living organisms present in the water, but this is from an hygienic point of view of the greatest importance. In its action it is far more reliable than any process of filtration, and should be invariably resorted to in the case of waters which bear any suspicion of sewage contamination. The vapid taste of the boiled water may be removed by passage through a filter, which, however, should be exclusively employed for this purpose and not for filtering unboiled water. A convenient form of apparatus for sterilising large quantities of water—*e.g.* for hospitals, barracks, &c.—is described by Miquel (Manuel d'Analyse bactériologique des Eaux, Paris, 1891, 188). The more extensive use of boiled instead of filtered water is one of the chief sanitary desiderata of the day. Although absolute sterility cannot be *guaranteed* by a few minutes' ebullition, yet the reduction in the number of microbes by this simple process is so great that it may be safely regarded as ample for practical purposes. Thus Miquel and Wada (*ibid.* 185) found in the case of the Ourcq-canal water of Paris:

Temperature	Bacteria in 1 c.c.
14°C.	460,800
50° for 10 minutes	600
60° ,,	(60)
70° ,,	88·8
80° ,,	62·4
90° ,,	26·4
100° ,,	·5
100° for 20 minutes	0·0

WATER FOR INDUSTRIAL PURPOSES.

Of the numerous uses to which water is put in industrial purposes, the most general and important is the raising of steam. The composition of the water supplied to steam-boilers is a matter of great consequence, as the use of unsuitable water may cause the corrosion of boiler-plates and the formation of deposits, which not only occasion a serious loss of heat but may also lead to most disastrous explosions.

Pure water—especially such as is rich in dissolved oxygen and carbonic anhydride—has a corrosive action on iron, which is increased by the simultaneous presence of chlorides. This corrosion is generally most marked where the above gases are longest in contact with the boiler-plates, thus especially in the vicinity of the cold-water feed, and at the water-line. The action is also more pronounced in the case of boilers which are used intermittently and not constantly (D. P. J. 1875, 218, 75; 1876, 219, 526).

Magnesium chloride is one of the commonest ingredients in natural waters, causing boiler-corrosion. Its action is due to the decomposition which its solutions undergo at high temperatures into oxychloride and hydrochloric acid, the latter escaping with the steam, and thus doing further mischief in the steam-pipes, valves, cylinders, &c. This action is to a considerable extent counteracted, although often by no means overcome, through the simultaneous presence in the water of the carbonates of the alkalis and alkaline earths. Sulphuretted hydrogen in water, as might be expected, causes the corrosion of iron plates; similarly injurious are moorland waters of acid reaction, acid waters generally, and waters containing much iron.

Boilers are also frequently corroded through the use of condensed water which contains some of the lubricants employed in the valves, cylinders, &c., through which the steam has passed, for, if animal or vegetable fats and oils have been employed in lubrication, these become decomposed by the steam, with liberation of free fatty acid.

Boiler deposits. These are formed through the use of impure feed water, and exhibit great variations, both in chemical and physical character, according to the nature of the water and the circumstances under which it is employed. Thus sea water gives rise to boiler incrustations, consisting principally of calcium sulphate and magnesium hydrate, the relative proportions of which appear to depend upon the pressure under which it is used. Thus Wallace (Iron, 1876, 427) gives the following results of analysis of the deposits from five marine boilers working under the specified pressures:

Composition of Marine Boiler Deposits.

Pressure in Atmospheres	·34	·4–·7	·7	1–1·2	1·4
Calcium sulphate	33·95	66·88	69·77	74·21	72·85
Magnesium oxide	40·05	18·96	15·75	14·95	13·18
Calcium carbonate	—	0	3·44	—	·34
Sodium chloride	trace	trace	·99	2·04	2·16
Ferric oxide, alumina, and calcium phosphate	1·33	·50	1·36	1·34	2·40
Silica	trace	trace	·16	·57	·80
Water and traces of carbonic anhydride	24·67	11·66	8·25	6·89	8·27
	100·00	98·00	99·72	100·00	100·00

Composition of Boiler Deposits and Feed Waters.

Pressure in atmospheres	2·5–3	3	3·5	3·5	—	about 2	5–6	3·5
Lime (CaO)	44·38	34·13	36·43	44·32	38·20	40·07	46·27	49·54
Magnesia (MgO)	·82	6·69	2·64	4·90	3·02	·25	5·59	1·78
Ferric oxide and alumina	2·24	5·28	1·67	2·10	·52	trace	2·44	1·48
Sulphuric acid (SO_3)	28·22	37·04	45·21	18·76	48·41	56·94	·95	5·82
Carbonic acid (CO_2)	19·25	6·09	3·66	24·48	3·40	trace	35·66	34·50
Silica	·47	trace	·88	trace	—	—	·87	1·07
Water given off under 120°C.	—	—	·41	—	·71	1·07	—	—
,, ,, ,, over 120°C.	3·68	7·90	3·04	2·31	3·50	·68	2·47	1·06
Insoluble matter	·48	2·25	5·65	2·46	1·91	—	4·65	2·47
Essential Composition.								
Anhydrite ($CaSO_4$)	—	—	49·98	31·96	50·44	90·44	1·63	9·86
Calcium sulphate ($2CaSO_4,H_2O$)	50·75	67·14	29·73	—	30·30	—	—	—
Gypsum ($CaSO_4,2H_2O$)	—	—	—	—	4·27	8·60	—	—
Calcium carbonate ($CaCO_3$)	44·25	14·65	8·30	55·65	8·20	—	81·45	81·10
Magnesium hydrate	1·19	9·69	3·83	7·11	4·36	—	8·10	2·58
Feed water; parts per 100,000.								
Lime deposited on boiling	22·5	8·6	trace	6·3	14·6	trace	—	—
Magnesia deposited on boiling	1·9	·3	0	3·9	0	0	—	—
Lime total	45·0	14·7	4·6	15·5	24·4	59·9	—	—
Magnesia total	8·5	2·2	·9	6·8	3·2	8·1	—	—
Sulphuric acid (SO_3)	21·9	12·1	4·0	8·9	23·2	30·6	—	
Chlorine	29·3	5·9	—	9·1	·9	77·0	—	—

Ordinary fresh waters give rise to deposits consisting principally of calcium carbonate and sulphate. Fischer (Technologie d. Wassers, Brunswick, 1880, 219) gives the composition of an interesting series of such deposits together with the composition of the feed waters from which they were obtained.

These deposits may thus consist almost exclusively of carbonate or of sulphate of lime, but more commonly of both, and it is generally found that waters containing a considerable proportion of sulphate in addition to the carbonate of lime give rise to the hardest and most troublesome forms of deposit, whilst waters containing carbonate only often deposit the latter in the form of a fine sediment, which, if frequently blown off, does not adhere to the boiler. It is often attempted to prevent these incrustations by means of substances added to the water in the boiler, which go by the name of *anti-incrustators.* Of these substances may be mentioned (1) *saline ones*, including soda-crystals, soda-ash mixtures of common salt and sulphuric acid, barium chloride, tribasic sodium phosphate, and sulphites; (2) *fatty* ones, including tallow and low-class oils; (3) *paraffin and paraffin products*, including paraffin oil, and soda-tar obtained in the purification of crude paraffin oil; (4) *other organic compositions*, including peat, moss, potatoes, glycerin, charcoal, tannin, &c. Although some of these anti-incrustators may be used with advantage under special circumstances, they are as a class to be condemned as either worthless or actually deleterious and entirely wrong in principle, inasmuch as the purification of the water is far better effected before it is allowed to enter the boiler. (See also W. I. Macadam, S. C. I. 1883, 12–21, and Fischer, Technologie d. Wassers, 236, 245.) For the methods of purifying water for industrial purposes, see below (p. 977).

Water for other industrial purposes. (1) For *brewing*, the composition of water employed is of highest importance. For all classes of beer it is essential that the water should be free from decomposing organic matter; such water is already injurious in the steeping of the barley, being liable to give rise to putrefaction and mould-growths, whilst in the subsequent brewing operations it tends to interfere with the purity of the fermentation, and impairs the keeping properties of the beer. For this reason the purest available water, preferably that from deep wells and springs, is invariably employed by brewers. As regards the mineral ingredients, it depends upon the kind of beer that is to be produced. Thus whilst a soft water is most advantageous for stout, porter, and the darker-coloured beers, for brewing pale ale it is necessary to employ a water containing not less than about 30–40 parts per 100,000 of calcium sulphate. It is the presence of this ingredient in the well waters of the New Red Sandstone around Burton-on-Trent that originally rendered that place famous for pale ale, but it is now customary to add gypsum to the water in places where the natural supply is deficient in this ingredient (*v.* Brewing). In this manner the magnificent supplies of water from the chalk and Oolite formations, which are rich in calcium carbonate but contain very little calcium sulphate, can be artificially rendered of equal quality for pale ale brewing to the Burton waters. The water obtained from the chalk beneath the London clay generally contains little or no lime at all, but a notable proportion of sodium carbonate, and is specially well adapted for brewing porter and coloured beers, as well as for distilleries. For distillery brewing a pure and soft water supply, although desirable, is by no means such a *sine quâ non* as for beer brewing, and it is within the knowledge of the writer that one of the largest and most successful distilleries employs highly-contaminated and brackish river water which would be utterly unfit for use in a brewery. For use in bakeries, the water should be in all respects of the same degree of purity as is demanded for drinking purposes.

For influence of water on brewing and distilling, *v.* also Lintner, Bierbrauerei; Griessmayer, Bierbrauerei; Stammer, Die Branntweinbrennerei; Märcker, Spiritusfabrikation; Laer, Zeitsch. f. angewandte Chem. 1890, 410; and Fischer, Technologie d. Wassers, and Das Wasser, seine Verwendung, Reinigung and Beurtheilung, Berlin, 1891.

(2) For the *textile industries* the water employed is often of the greatest consequence. Thus in bleaching and dyeing the presence of iron and manganese, even in very small quantities, is highly deleterious, giving rise to iron and manganese stains on the bleached goods, and causing spots and modifications in the shades of dyed materials. Hard water, again, involves the use of larger quantities of alkali and soap in the several operations of boaking, scouring, and milling, and the insoluble lime-soap is left adhering to the fibre, often preventing the subsequent application of mordant or dye. In those operations, again, in which dyed fabrics are soaped, the lime-soap often injures the brilliancy of the colour, whilst in other cases the earthy soaps precipitated on the fibre act as mordants, and attract the colouring matters on those parts of the goods where it is not wished to fix them. In general, hard water has the effect of dulling many colours, and if due to bicarbonates retards, or even prevents, the dyeing of such colours as require an acid bath (*e.g.* cochineal scarlet). In some cases hard water containing bicarbonates wastes the mordants by precipitation in the bath instead of on the fibre, whilst it is sometimes actually beneficial for the washing of goods which have been mordanted with basic mordants. Such water is unsuitable for the solution of many coal-tar colours—*e.g.* methyl violet—a portion of the latter being lost as a tarry precipitate, whilst the goods are often spotted. For dyeing with some colours—*e.g.* alizarin and logwood—the presence of a certain amount of lime is almost indispensable; a pure water to which a known quantity of lime-salt has been added is, however, preferable to a naturally hard water, especially if the latter is of variable composition. Water containing alkaline carbonates is sometimes advantageous, *e.g.* in wool-scouring, and in those dyeing operations in which the addition of sodium carbonate is prescribed; but in mordanting, in the dyeing with many colours, and in the washing of dyed goods, it is often very prejudicial; in these cases it should be neutralised with sulphuric or acetic acid. Acid waters are generally highly injurious, and should be neutralised with sodium carbonate. Sulphuretted hydrogen in water is also very objectionable in many operations of dyeing, more especially in mordanting with metallic salts (Hummel, Dyeing of Textile Fabrics). For the manufacture of *paper*, water containing iron is highly objectionable, giving rise to stains, whilst the presence of hardness is objectionable in causing the decomposition of the rosin-soap.

(3) For *tanning*, pure water is also a desideratum. Water much contaminated with organic matter causes injury to the surface of the leather, and sometimes a corrosion from the flesh-side of the skin. Water containing carbonic acid, or the bicarbonates, or calcium and magnesium sulphates, causes the hides to swell, whilst the chlorides prevent the swelling, and hence sea water cannot be employed for the purpose. Hard water occasions a less perfect utilisation of the tanning materials, and an excess of chlorides retards the tanning process and causes the leather to attract moisture; the presence of iron is not so objectionable as is commonly supposed (Fischer, Das Wasser, 49–51).

(4) In *sugar-refining*, the sulphates and alkaline carbonates are more productive of molasses than the chlorides, whilst nitrates are specially objectionable, as they prevent the crystallisation of six times their weight of sugar (Fischer, Technologie d. Wassers, p. 286).

Purification of water for industrial purposes.

As already pointed out, some substances, although unobjectionable in drinking water, operate prejudicially when the water is employed for many industrial purposes, and numerous methods have been devised for removing these impurities or for counteracting their effects. Amongst the crudest and most unsatisfactory of these endeavours is the use of anti-incrustators for steam boilers, to which reference has been already made. But few methods of purification have found favour in actual practice, and to these alone will any attention be given here. The processes which have for their object the removal of matters in suspension and organic substances have been already described under *Purification of drinking water* (*v.* p. 971), whilst the processes intended for the improvement of industrial water supplies are chiefly directed to the removal of lime and magnesia salts in solution, which, as has been shown above, interfere with the success of so many industrial operations. This removal of lime and magnesia salts is frequently spoken of as 'water-softening,' in consequence of the water after such treatment requiring less soap when used for washing purposes.

Purification with lime (Clark's process). This beautiful method of purification was first proposed by the late Dr. Clark, of Aberdeen, in 1841, and consists in the decomposition of the bicarbonate of lime or 'temporary hardness' of water by the addition of a suitable quantity of slaked lime, according to the equation

$$\underset{\text{Calcium bicarbonate}}{CaH_2(CO_3)_2} + Ca(OH)_2 = \underset{\text{Calcium carbonate}}{2CaCO_3} + 2H_2O.$$

Thus both the lime in solution as bicarbonate as well as that added in the form of hydrate are precipitated as normal carbonate, which is almost quite insoluble in water. The calcium hydrate is sometimes added in the form of milk of lime, sometimes in that of clear lime-water, but the latter is far preferable, as the quantity added can be more easily controlled and an excess avoided. The necessary quantity of calcium hydrate is most easily ascertained by adding such an amount that, after thorough mixing, a small quantity of the water taken out yields a yellow or brown colour with a solution of silver nitrate, thus indicating that an excess of calcium hydrate is present; more water is then added, until, on similarly testing, no colouration with the silver nitrate is obtained. This test should invariably be resorted to even in the case of such waters as are of very constant composition, and which, therefore, admit of the lime being proportioned by experience, as otherwise an excess or deficiency of lime is nearly sure to result. In its original form the Clark process is carried out in large tanks in which the water can remain at perfect rest for about sixteen hours, although by the use of a floating exit-pipe the clear surface water can often be drawn off after two or three hours, and before the whole of the precipitate has reached the bottom. This method has been most successfully employed on a large scale at the Colne Valley Waterworks, near Bushey, at Canterbury, Caterham, and many other places on a small scale. The 'temporary hardness' only is, of course, removed, and even this not completely, as under the most favourable circumstances a small proportion of calcium carbonate remains in solution, whilst in the case of waters containing bicarbonate of magnesia the removal of the latter is generally far less complete (*v.* analyses, p. 969). In addition to these bicarbonates, the salts of iron and much organic matter are also removed.

In order to obviate the large amount of storage capacity required for Clark's process, several modifications have been introduced, in which the precipitate formed by the treatment with lime is either removed by filtration or made to rapidly subside by artificial means. The most notable of these improved processes are the so-called 'Porter-Clark,' in which the precipitate is removed with a filter-press, and Gaillet and Huet's process, in which subsidence is promoted by causing the water to take a circuitous zig-zag and upward path after the addition of the lime. In this latter process both lime and caustic soda are frequently employed in conjunction as the softening agents; in this manner both 'temporary' and 'permanent' hardness can be, to a great extent, removed, thus:

$$CaH_2(CO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O$$
$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

In the table on p. 969 will be found the analytical results obtained by the writer in his examination of the water supplies of Wellingborough, Southampton, London (New River Company), and St. Helens before and after softening with lime, as well as of the water of a deep well at Victoria Dock, London, before and after treatment by Gaillet and Huet's process.

Magnesia has also sometimes been employed to a limited extent for softening instead of lime. Under these circumstances the following reactions may take place, especially if heat is applied:

$$CaH_2(CO_3)_2 + MgO = CaCO_3 + MgCO_3 + OH_2$$
$$MgCO_3 + CaSO_4 = CaCO_3 + MgSO_4$$
$$MgCO_3 + CaCl_2 = CaCO_3 + MgCl_2$$

(Fischer, Chem. Technol. d. Wassers, Brunswick, 1880, 264).

The formation of magnesium chloride is obviously disadvantageous for boiler purposes.

A number of other processes of chemical purification have from time to time been suggested, but none of them have met with any great success. Thus attempts have been made to utilise the following reactions:

$$CaH_2(CO_3)_2 + Ba(OH)_2 = CaCO_3 + BaCO_3 + 2OH_2$$
$$CaSO_4 + Ba(OH)_2 = BaSO_4 + Ca(OH)_2$$
$$CaSO_4 + BaCl_2 = BaSO_4 + CaCl_2$$
$$CaH_2(CO_3)_2 + \underset{\substack{\text{Sodium}\\\text{oxalate}}}{C_2O_4Na_2} = \underset{\substack{\text{Calcium}\\\text{oxalate}}}{C_2O_4Ca} + \underset{\substack{\text{Sodium}\\\text{bicarbonate}}}{Na_2H_2(CO_3)_2}$$
$$CaSO_4 + C_2O_4Na_2 = C_2O_4Ca + Na_2SO_4$$
$$CaCl_2 + C_2O_4Na_2 = C_2O_4Ca + 2NaCl$$
$$CaH_2(CO_3)_2 + 2HCl = CaCl_2 + 2CO_2 + 2OH_2$$

For the effect of softening processes on the bacteria in water, *v.* p. 973.

The action of water on lead, zinc, and copper. The action of water on these metals, and especially on lead, is of great importance in connection with the distribution and storage of water. The Romans already employed leaden pipes, and Vitruvius and Galen were aware that some waters were thereby rendered deleterious. On the other hand, some waters have so little action on lead that pipes of this material have been in use for upwards of 200 years without showing any trace of corrosion (Fischer, Technologie d. Wassers, 317). As to the cause of this great difference in the behaviour of waters towards lead, the most varied opinions have from time to time been expressed, nor is there even now any great unanimity on the subject. As a general rule, hard waters, and more especially those containing bicarbonates, do not act on lead; the greater number of active waters are soft, and generally entirely destitute of bicarbonates, but by no means all such waters act on lead. The activity has been ascribed by different authorities to the presence or absence of a great variety of ingredients in the water—*e.g.* the presence of dissolved air (Yorke), ammonium nitrite (Medlock), ammonium carbonate (Böttcher). Some have contended that organic matters diminish the activity (Horsford), others that they increase it (Hofmann, Graham, Miller, and Noad). The latter authorities are of opinion also that the presence of dissolved oxygen and the absence of more than three volumes of carbonic anhydride in 100 vols. of water are amongst the conditions necessary for the attack upon lead. It has also been contended that a minute proportion of phosphate of lime prevents a soft water from attacking lead (Riv. Pollut. Commiss. 6th Rep. 224), whilst according to others, again, the protecting ingredient is silica (Crookes, Odling, and Tidy, Report on the Action of Water on Lead, London, 1886). In many cases the activity of the water is due to the presence of organic acids (Allen), this being doubtless a fruitful cause of moorland waters acting on lead. The activity of many waters is confined to new untarnished lead, whilst others continue to act, sometimes with increased vigour, on the old and tarnished metal (P. F. Frankland, The Action of Water on Lead, S. C. I. 1889, 241).

Numerous expedients have been resorted to in order to destroy this activity of some soft waters. When acidity is the presumable cause the most obvious remedy is the filtration of the water through finely-divided limestone; in practice, however, this is found to be only of temporary service, as the surfaces of the limestone become coated with a film which prevents their being further acted on by the water. It has been found more effective to continuously mix the water with a milk of finely divided carbonate of lime, and allowing this to subside before the water is distributed. The writer has found a most efficient method of dealing with active waters to be the addition of a small proportion of carbonate of soda (*l.c.*). It is obvious from his experiments, moreover, that the activity of some moorland waters is not occasioned by acidity at all, and that in all probability in such cases it is due to the particular kind of organic matter present, the lead-dissolving properties of which are not overcome until a certain excess of the sodium carbonate has been added. With a view of communicating silica to the water, Crookes, Odling, and Tidy (*l.c.*) have employed filtration through a composite filter, consisting of 2 feet sand at the top, followed by 1 feet 3 inches broken flints in the middle, and 1 foot 3 inches of limestone at the bottom, the activity of the water being thereby very considerably diminished; it is doubtful whether, however, the efficiency of such filters can be maintained without frequent renewal. In carrying out similar filtration the writer has been able to confirm the marked reduction in the activity of the water, but he has found the proportion of silica to be hardly influenced by the filtration. From what has been said above, it is obvious that although the chemical composition of a water may indicate the probability or improbability of its acting on lead, recourse should invariably be had to actual experiment in order to finally determine this point, whilst the seasonal variations in the character of surface waters should also be duly taken into consideration in such investigations. Experience has also shown that some waters act powerfully on lead when the pipes are charged intermittently, whilst the action becomes very much diminished if they are kept under constant pressure. The effect of pressure on the activity ought, therefore, always to be specially determined (P. F. Frankland, S. C. I. 1889).

Some polluted waters have a very strong and continued action on lead (Riv. Pollut. Commiss. 6th Rep. 226), and in such cases the obvious remedy is the abandonment of the source.

It is worthy of note that hot water generally acts much more violently on lead than cold, and further that the lead dissolved in water is entirely removed by passage through any of the numerous forms of animal charcoal filters.

As regards the quantity of lead in water from which danger to health is to be apprehended, it is now generally admitted that water containing anything above one-twentieth grain of lead per gallon, or ·07 part per 100,000, may, by continued use, produce mischief.

Of the action of water on zinc but little is known beyond the fact that many waters do act on it, and that it is therefore not to be recommended for the construction of cisterns &c. in which drinking water is to be stored. The solution of the zinc takes place with special facility if metallic iron is also in contact with it (Heaton, C. N. 49, 85; P. F. Frankland, *ibid.* 115; Stevenson, *ibid.* 107).

Copper appears to be continuously acted on by water, especially if simultaneously in contact with air, and hence should not be used in connection with drinking water.

The Chemical Analysis of Water.

As the qualitative analysis of the ingredients of water is of no practical importance, and involves no special methods, the quantitative examination will alone be considered here. In order that the analysis may be of any value, especially for sanitary purposes, it is of the greatest importance that the samples should have been collected with care, and to this end the following instructions should be adhered to.

Instructions for the Collection of Samples.

1. Stoppered glass bottles of the kind technically known as 'Winchester quarts,' and procurable from any druggist, should be used for this purpose. These bottles hold about two imperial quarts, and must be perfectly clean; it is desirable that they should not have been previously used for any other purpose.

Waters for analysis must not be put into stoneware jars. Corks should also be avoided if possible, but if used they ought to be quite new and well washed with the water before insertion into the bottle.

2. Before collecting the sample, rinse the bottle well three times with the water, filling it each time about one-third full. Then fill it to within half-an-inch of the stopper, tie the stopper tightly down with a piece of calico over it, and seal the string.

If the sample be taken from a well with a pump fixed in it, pump about four gallons of water before filling the bottle; then pump the water directly from the spout of the pump into the bottle.

If the sample be taken from a tap, let a couple of gallons flow before filling the bottle, then allow the water to flow directly into the bottle from the tap.

If the sample be intended to represent the water supply of a town, it ought to be taken from a pipe in direct communication with the street main, and not from a cistern or from any pipe supplied from a cistern.

In taking a sample of water from a tank well (in which a pump is not fixed), or stream, plunge the neck of the bottle completely below the surface when practicable; and if a can or dipper be used, let it and the string used in drawing it up be scrupulously clean, and avoid, as much as possible, collecting the water from the surface. On the other hand, be careful not to disturb any mud or sediment at the bottom of the water.

3. The following are the *minimum* quantities of water necessary for such analyses as are required for sanitary purposes:—

Sewage. Polluted rivers and streams. Shallow well waters.	One Winchester quart.
Deep wells. Ordinary unpolluted rivers, streams, and springs.	Two Winchester quarts.

Lakes and tarns. Mountain springs and streams.	Three Winchester quarts.

At the time the samples are forwarded for analysis, give the following particulars :—

(*a*) From what source the samples are collected—wells, rivers, or streams.

If from wells,

(*b*) Describe the soil and subsoil, and also the water-bearing stratum into which the well is sunk.

(*c*) The diameter and depth of well.

(*d*) The distance of the well from either cesspools or drains.

If from rivers or streams,

(*e*) State the distance from the source to the point at which the sample is collected.

(*f*) State whether sewage or other animal-polluting matter is known to gain access to the river or stream above the point at which the sample is collected.

If from springs,

(*g*) Describe the stratum from which the spring issues.

(*h*) State whether the sample is taken direct from the spring or otherwise.

Suspended matter. The suspended matter, if considerable in amount, should be separately determined, but if only present in minute quantity it is advisable to regard it as part of the dissolved matter, in which case it is necessary that the sample should be well shaken before taking out each portion for analysis, so that the suspended particles may be uniformly distributed. If it is decided to determine the suspended matter separately, the sample should be well shaken, and 250 or 500 c.c. measured out and passed through a filter previously dried, and weighed at 100°C. The matter on the filter is washed with distilled water, and dried at 100°C. until of constant weight. Some analysts prefer to dry at 105°, 110°, or even 120°C., but in all cases the temperature should be specified. The filter and its contents are then incinerated in a coil of platinum wire and dropped into a weighed platinum crucible, gently ignited until free from organic matter, and then treated with a few drops of a solution of ammonium carbonate, and dried at 150°C. The loss in weight represents organic matter and water of hydration. It is sometimes of importance to determine the proportion of carbon to nitrogen in the organic part of the suspended matter. For this purpose some of the suspended matter is collected on an ignited plug of asbestos or glass wool, transferred to a small flask, and boiled with 20 c.c. of sulphurous acid and some distilled water free from ammonia and organic matter, and then further treated, as in the determination of organic carbon and nitrogen, by the combustion process (*v.* p. 986). If the suspended matter has been thus separately determined, the remainder of the analysis should be performed on the water, after filtration through Swedish paper, rejecting the first 250 c.c. which pass through, or if the suspended matter completely settles on standing the clear water may be siphoned off. The suspended matter may, of course, in exceptional cases also have to be submitted to a complete mineral analysis, or examined for some special ingredient.

MATTERS IN SOLUTION.

Total solids. 250 or 500 c.c. of the water are evaporated to dryness in a weighed platinum dish on a water- or steam-bath, the dish being supported on a glass or porcelain, but not on a metallic, ring. The dish and residue are then dried until constant at 100°, 105°, 110°, 120°, or even at 180°C. Some analysts further determine the loss after ignition and subsequent treatment with ammonium carbonate. There is, however, but little value in this determination, which affords only the very crudest indication of the amount of organic matter; indeed, some water residues actually increase in weight after ignition. The residue obtained as above may be further conveniently utilised for the determination of nitrates and nitrites by the mercury method (*v. infra*).

Ammonia. A measured volume of the water (varying from 100–1000 c.c., according to the proportion of ammonia present) is distilled in a capacious flask or retort connected with a Liebig's condenser, about 1 grm. of recently ignited sodium carbonate having been previously added. It is essential that the whole apparatus should have been carefully freed from ammonia immediately before use, which can be done by similarly distilling some water in the apparatus until the distillate gives no reaction with Nessler solution. The remainder of the water in the flask or retort is then thrown away, and the measured quantity of the sample under examination introduced along with the sodium carbonate. The distillation should be carried on briskly, and the distillate collected in colourless glass cylinders of 50 c.c. capacity. If less than 500 c.c. has been used, this volume should be made up with distilled water free from ammonia before distillation. If the quantity of water has been well chosen, the whole of the ammonia will be found in the first three cylinders of the distillate, whilst in most cases it will be all contained in the first. The quantity of ammonia in each cylinder is estimated by adding 1 c.c. of Nessler solution, and comparing the colouration obtained with that similarly produced by known quantities of a standard solution of ammonium chloride, added to 50 c.c. of distilled water free from ammonia. The Nessler reaction is so delicate that by its means 1 part of NH_3 in 100,000,000 parts of water can be easily detected. The colour produced by more than 10–15 c.c. of a solution of NH_4Cl (containing ·00001 grm. NH_3 per litre) is too deep for accurate comparison, and should one of the cylinders require more than this the determination must be repeated on a smaller volume of water. This may be generally avoided, however, by adding the Nessler solution to the second and third cylinders of distillate before the first, and if it is found that the second cylinder gives a colour requiring more than 5 c.c. of the above solution of ammonium chloride for its imitation the first cylinder should be diluted, and an aliquot part taken for testing with the Nessler.

The Nessler solution is prepared by dissolving 62·5 grms. of potassium iodide in 250 c.c. of distilled water; set aside 10 c.c. of this, and run into the remainder a cold saturated solution of mercuric chloride until a permanent precipitate is formed, then add the above 10 c.c. of potassium iodide, which will cause its solution, after which very carefully add more of the mercuric chloride until a slight precipitate remains on stirring. Now add 150 grms. of potassium hydrate dissolved in distilled water, and dilute the whole to 1,000 c.c. After settling, decant the clear liquid into a bottle for use.

For modifications (Miller, Fleck, Tromsdorff, Hehner) of the above method, *v.* 'Untersuchung d. Wassers,' Tiemann and Gärtner, Braunschweig, 1889.

As the 'albuminoid ammonia' is commonly determined in one operation with the 'free' ammonia, the method of estimating the former will be now described, instead of considering it under the methods for determining organic matter, where it more properly belongs.

'*Albuminoid ammonia*' *process.* Whilst the determination of the free ammonia is being proceeded with as above, the solution of alkaline permanganate must be prepared for this process, as it is required immediately the free ammonia has passed over. The volume of the alkaline permanganate (for preparation *v.* below) taken must be at least one-tenth of the volume of the sample being distilled for ammonia, and it should not exceed that volume unless the water contains a very large amount of organic matter. The alkaline permanganate taken is then diluted with four times its volume of distilled water, and boiled in a flask during the whole of the time that the distillation for free ammonia is going on as above, and when the latter is finished it is added to the water remaining in the distilling flask or retort (the whole volume in this must now be not less than 500 c.c.), and distillation is then continued until the distillate is free from ammonia. The distillate is collected and Nesslerised, as in the determination of free ammonia above. The ammonia thus evolved by distillation with alkaline permanganate is generally recorded as 'albuminoid ammonia' (*v.* p. 988). The alkaline permanganate solution is prepared by dissolving 200 grms. of potassium hydrate and 8 grms. of pure potassium permanganate in 1,100 c.c. of distilled water, then boiling the solution rapidly until concentrated to about 1,000 c.c.

Chlorine. (*a*) *Mohr's method.* 50 or 100 c.c. of water are treated with a few drops of a solution of potassium chromate, and a standard solution of silver nitrate is then run in from a burette until the precipitate becomes of a faint but distinctly red colour. The water must be well agitated after each addition of the nitrate, the reaction depending upon the decomposition of the red silver chromate by dissolved chlorides with formation of silver chloride and soluble chromate. As soon as the last trace of chloride is precipitated as silver chloride, the red colour of the silver chromate makes its appearance. By using a solution of silver nitrate containing 2·3944 grms. per litre, the number of c.c. employed gives at once (if 50 c.c. of water have been taken) the parts of Cl per 100,000, whilst if 100 c.c. of water are taken the silver nitrate solution should be of double this strength.

Mohr's method cannot be employed if the water is acid, and if this is the case a given volume of the water should be boiled with an excess of pure calcium carbonate (free from chlorides), filtered, the filtrate made up to known volume, and the chlorine determined in a part of this. In the presence of reducing substances, much organic matter, sulphuretted hydrogen, and sulphites, the method is also inapplicable, and in such cases it is desirable to determine the chlorine gravimetrically, which should also be done if the proportion of chlorine is large.

(*b*) *Volhard's method.* 50 or 100 c.c. of the water are treated with an excess of decinormal silver nitrate, the mixture being well agitated so as to cause the silver chloride to settle in flakes; then about ten drops of a cold saturated solution of iron-alum are added, and subsequently enough strong nitric acid (free from nitrous acid) to remove the colour of the ferric salt. Decinormal ammonium sulphocyanate is then added from a burette, stirring well all the time, until the liquid acquires a light-yellow brown colour, which remains permanent on leaving the liquid at rest for about ten minutes. By deducting the number of c.c.'s of sulphocyanate from that of the silver nitrate added, the remaining silver nitrate indicates the proportion of chlorine present in the water. The advantage of this method consists in its being applicable to acid liquids. The method depends upon there being no formation of red ferric sulphocyanate until the whole of the silver in solution has been precipitated as sulphocyanate (A. 190, 24).

Nitrogen as nitrates and nitrites. A number of different methods have been devised for the determination of oxidised nitrogen; there are, however, only a few which have been largely adopted in practice, and such alone will be described here.

(*a*) *Crum's method.* This depends on the decomposition which nitrates and nitrites undergo when dissolved in strong sulphuric acid on being shaken up with mercury, and which leads to the evolution of the whole of the nitrogen as nitric oxide, the volume of which is then determined. The residue obtained in the estimation of the total solids (see p. 980) may be conveniently used for this determination also. This residue in the platinum or glass dish is repeatedly treated with a very small quantity of hot distilled water, which is brought into thorough contact with the residue by detaching the latter with a small glass rod covered with a piece of india-rubber. The aqueous extracts, which should in all not exceed about 10 c.c., are passed through a small filter and collected in a little beaker. This aqueous extract, containing all the soluble salts in the water residue, is evaporated nearly to dryness on a water-bath, after which it is dissolved again in a minimum quantity (1 or 2 c.c.) of water, and introduced into a Lunge nitrometer (Berliner Berichte, xi. 434); the beaker is repeatedly rinsed with a few drops of hot water, and these rinsings added to the nitrometer. The beaker is then further rinsed with pure strong sulphuric acid (free from oxides of nitrogen), and this also is transferred to the nitrometer. About 1½ volumes of sulphuric acid must in all be used to 1 volume of aqueous extract. If the water contains soluble carbonates there will be an evolution of carbonic anhydride when the sulphuric acid mixes with the aqueous extract; the gas should be allowed to collect *without shaking the tube*, and should then be expelled. The contents of the nitrometer tube are now violently agitated with the mercury, and then in the course of a minute or so the evolution of nitric oxide will commence, and the agitation should be continued as long as any gas continues to come off. If the water contains a considerable quantity of chlorides some hydrochloric acid may have been given off along with the nitric oxide, but this may be removed by admitting a little water into the nitrometer. When the gas has cooled to the temperature of the air, its volume is measured at atmospheric pressure. The determination is rendered more accurate, especially if the quantity of nitrates and nitrites is only small, by measuring the nitric oxide in Frankland's gas apparatus, in which case the decomposition with mercury and sulphuric acid is effected in a small tube standing in a mercury trough, the evolved nitric oxide being then transferred to the gas apparatus (*v.* Frankland's Water Analysis, or Agricultural Chemical Analysis, P. F. Frankland; also S. C. I. 1868, 106, or Sutton's Volumetric Analysis). This method, which is by far the most convenient for ordinary water analysis, becomes inapplicable in the presence of very large quantities either of organic matter or of chlorides.

(*b*) *Methods of Schulze-Tiemann, and of Schlösing-Reichardt*, depend upon the decomposition of nitrate and nitrites by ferrous chloride and hydrochloric acid, and the measurement of the evolved nitric oxide. Of these methods, which closely resemble each other, the former, as the more convenient, need be alone considered here.

100–500 c.c. of the water are concentrated by evaporation to about 50 c.c., which are then introduced into a flask of about 150 c.c. capacity, provided with an india-rubber stopper, perforated by two narrow pieces of glass tubing, of which one (A) extends about an inch into the flask, and is constricted below, whilst the other (B) only just penetrates the stopper; the tube (B) is externally connected by means of a short piece of india-rubber tubing provided with a pinch-cock, with a delivery tube dipping into a trough containing 10 p.c. caustic soda solution previously boiled to expel air. The tube (A) is also connected with india-rubber and pinch-cock to another piece of glass tubing, which is allowed to hang vertically downwards. The water in the flask is vigorously boiled with the pinch-cocks open until the air is completely expelled by the steam, then the pinch-cock on (B) is closed whilst that on (A) is left open until the volume of water in the flask is reduced to about 10 c.c.; this pinch-cock is then also closed, and the flame removed from beneath the flask. The glass tube attached to (A) is carefully filled with water up to the pinch-cock; 15–20 c.c. of a saturated solution of ferrous chloride are introduced into the flask, in which there is now a partial vacuum, by siphoning from a small beaker through (A), the pinch-cock being temporarily opened, and about an equal quantity of strong hydrochloric acid is made to follow in the same manner into the flask. The flask is now carefully heated, and when the internal pressure rises the pinch-cock on (B) is opened, and the evolved gas allowed to pass through the delivery tube into a measuring tube filled with the 10 p.c. caustic soda solution standing in the trough. The heating of the flask is continued until the volume of gas in the measuring tube ceases to increase. The measuring tube is transferred to a tall glass cylinder full of water, and after the gas has fallen to the temperature of the room the volume is measured at the atmospheric pressure, a correction being of course made for the tension of aqueous vapour.

This method is specially applicable in the case of water containing excessive quantities of organic matter and chlorides (B. B. 1873, 1041; Tiemann and Gärtner's Untersuchung d. Wassers, 170).

For Schlösing-Reichardt's method, *v.* Zeitsch. f. analyt. Chem. 1870, 24, or Tiemann and Gärtner's Untersuch. d. Wassers, 175.

(*c*) *The aluminium and zinc-copper couple methods* depend upon the conversion by nascent hydrogen of the oxidised nitrogen in the water into ammonia, and estimation of the latter by Nessler solution.

Aluminium method. 100 c.c. of the water are introduced into a flask together with 10 c.c. of caustic soda solution free from nitrates and nitrites, the mixture being boiled until it is reduced to about one-fourth of its volume. It is then diluted to about its original bulk with distilled water free from ammonia, and a piece of aluminium foil, about two inches square and wrapped round a piece of glass rod, is dropped into the flask, which is then fitted with a stopper and small U-tube containing glass beads moistened with hydrochloric acid free from ammonia. After the evolution of hydrogen has continued for about six hours, the glass beads and washings of the U-tube are transferred to the liquid in the flask; the latter is then attached to a Liebig's condenser, and the ammonia determined by distillation and Nesslerising in the ordinary way (see p. 980). According to Tiemann and Gärtner (Untersuchung d. Wassers, 208), only the equivalent of 72–90 p.c. of the nitric acid is thus recovered as ammonia.

Zinc-copper couple method. The residue obtained in the determination of 'total solids' is extracted with about 25 c.c. of hot distilled water, and this is boiled down with a fragment of recently-ignited pure lime about the size of a hemp-seed to one-fourth of its bulk. This liquid, together with the washings of the dish containing the residue, is transferred through a stoppered funnel into an eight-ounce Wurtz flask, attached to a Liebig's condenser, and containing the requisite amount of the zinc-copper couple. The distillation is carried on until the greater part of the water has passed over, after which hot distilled water is repeatedly run into the flask and the distillation continued until about 100 c.c. of distillate have been collected; the latter is then Nesslerised in the ordinary way (Thorpe, C. J. 1873, 541). According to Tiemann and Gärtner, from 88–95 p.c. of the nitric acid is thus obtained.

A rapid method of estimating nitrates in water has been recently devised by Harrow (C. J. 1891, 320), depending on the reduction to nitrite by zinc-dust and estimation of the nitrous acid by sulphanilic acid and α-naphthylamine (Griess' test). This reagent is prepared by dissolving 1 grm. of α-naphthylamine, 1 grm. sulphanilic acid, and 25 c.c. strong hydrochloric acid in about 200 c.c. distilled water; boil with a small quantity of animal charcoal, filter, and make up to 500 c.c. The process is conducted thus: 50 c.c. of the water are placed in a beaker of 100 c.c. capacity, and in three similar beakers 50 c.c. of three standard solutions of potassium nitrate, containing (1) 1·0 part N, (2) ·1 part N, (3) ·01 part N per 100,000; to each beaker 10 c.c. of the above test-solution are added, and afterwards a very small quantity (7–8 milligrams) of zinc-dust. If nitrate is present in the water a pink colour appears, which must be compared with that yielded by the three standard solutions after fifteen minutes. This gives an approximate idea of the amount of nitrate present, whilst in order to obtain an accurate result the water must be diluted until the colour produced is almost identical with that given by one of the standards. The results appear to be accurate, but it is especially necessary to avoid the addition of large quantities of zinc-dust, which would decolourise the solution.

(*d*) *The indigo method* differs from those previously described in being a simple volumetric method depending upon the decolourising action of nitric acid on indigo solution. The results are only accurate when the greatest uniformity is preserved in the conditions under which the experiments are made—the process is, in fact, entirely empirical. It may be carried out as follows: 25 c.c. of the water are mixed with 50 c.c. of pure strong sulphuric acid; a dilute solution of indigo is then immediately added from a burette, shaking the whole time, until the solution acquires a bluish-green colour. In a second experiment nearly the whole volume of indigo which was found necessary in the first experiment is added at once, and the blue colour is then obtained by further small additions, and in this manner, by shortening the time taken in the titration, a more accurate result, generally higher than in the preliminary experiment, is obtained. The solution of indigo must be standardised under precisely similar conditions by means of a solution of potassium nitrate of known strength. The indigo solution should be chosen of such strength that 6–8 c.c. correspond to ·001 grm. N_2O_5; and if 25 c.c. of the water contains more than ·003–·004 grms. N_2O_5, it should be diluted before a final titration is made. The method is only suitable for use by an operator in continual practice (Marx, Fr. 1868, 412; Trommsdorff, *ibid.* 1870, 171; Warington, C. J. 1879, 578; Water Analysis, E. Frankland, 31; Agricultural Chemical Analysis, P. F. Frankland). The results are also interfered with, becoming too low if there is a large amount of organic matter in the water.

The methods described above do not distinguish between nitrous and nitric acids. Indeed, the indigo method is altogether unreliable in the presence of any notable proportion of nitrous acid, as is also Crum's method, should it be necessary to allow any carbonic anhydride to escape before shaking with mercury (see p. 981). As nitrous acid is, however, generally only present in natural waters in minute traces, these difficulties do not frequently arise, and the nitrous acid may be most conveniently estimated by colorimetric methods, of which there are several in vogue. Of these may be mentioned:

(*a*) *Preusse-Tiemann's method*, depending upon the production of Bismarck brown when an acid solution of a nitrite acts upon metaphenylenediamine. 100 c.c. of the water are placed in a colourless glass cylinder, 1 c.c. of dilute sulphuric acid (1 : 3) is added, and then 1 c.c. of solution of *m*-phenylenediamine (5 grms. in 1,000 c.c. distilled water, decolourised if necessary with animal charcoal) if the colour appears in less than one or two minutes; the experiment must be repeated with a smaller quantity of water, in each case diluted, however, to 100 c.c. The colouration is then imitated under precisely similar conditions with a standard solution (the standardisation can be effected either by the potassium permanganate, or, better, by the urea method) of potassium or sodium nitrite. The final tint is not arrived at until the mixture in the glass cylinder has stood for twenty to twenty-five minutes, which is the great drawback of the process (B. B. 1878, 627; Water Analysis, E. Frankland, 40; Agricult. Chem. Anal., P. F. Frankland, 286; see also Warington, The Detection of Nitric and Nitrous Acids, C. N. 51, 1885, 39).

For larger quantities of nitrous acid, as also for the standardisation of solutions of sodium and potassium nitrite, the urea method devised by the writer is to be recommended (C. J. 1888, 364).

Hardness. The determination of the hardness of a water consists in empirically ascertaining the amount of soap which has to be destroyed by a given volume of the water before a lather can be obtained, and expressing this in terms of the amount of carbonate of lime which must be dissolved in the same volume of water to destroy the same amount of soap. Accurate results can only be obtained by preserving uniformity in the conditions of experiment.

50 c.c. of the water are measured into an 8 oz. stoppered bottle, which is then violently agitated and the air sucked out by means of a glass tube to remove any carbonic anhydride which may be given off by the water. A standard solution of soap (*v. infra*) is then added in diminishing quantities *not exceeding* ·5–1·0 *c.c. at a time, even at the first*, violently shaking after each addition, until the froth produced remains unbroken over the surface for a period of five minutes, when the bottle is placed at rest on its side. The quantity of carbonate of lime corresponding to the volume of soap solution employed can then be ascertained by reference to the following empirical table:—

Table of hardness in parts per 100,000, 50 *c.c. of water being used.*

C.c. of soap solution	$CaCO_3$ per 100,000	C.c. of soap solution	$CaCO_3$ per 100,000	C.c. of soap solution	$CaCO_3$ per 100,000
·7	·00	5·9	7·29	11·0	14·84
·8	·16	6·0	·43	·1	15·00
·9	·32	·1	·57	·2	·16
1·0	·48	·2	·71	·3	·32
·1	·63	·3	·86	·4	·48
·2	·79	·4	8·00	·5	·63
·3	·95	·5	·14	·6	·79
·4	1·11	·6	·29	·7	·95
·5	·27	·7	·43	·8	16·11
·6	·43	·8	·57	·9	·27
·7	·56	·9	·71	12·0	·43
·8	·69	7·0	·86	·1	·59
·9	·82	·1	9·00	·2	·75
2·0	·95	·2	·14	·3	·90
·1	2·08	·3	·29	·4	17·06
·2	·21	·4	·43	·5	·22
·3	·34	·5	·57	·6	·38
·4	·47	·6	·71	·7	·54
·5	·60	·7	·86	·8	·70
·6	·73	·8	10·00	·9	·86
·7	·86	·9	·15	13·0	18·02
·8	·99	8·0	·30	·1	·17
·9	3·12	·1	·45	·2	·33
3·0	·25	·2	·60	·3	·49
·1	·38	·3	·75	·4	·65
·2	·51	·4	·90	·5	·81
·3	·64	·5	11·05	·6	·97
·4	·77	·6	·20	·7	19·13
·5	·90	·7	·35	·8	·29
·6	4·03	·8	·50	·9	·44
·7	·16	·9	·65	14·0	·60
·8	·29	9·0	·80	·1	·76
·9	·43	·1	·95	·2	·92
4·0	·57	·2	12·11	·3	20·08
·1	·71	·3	·26	·4	·24
·2	·86	·4	·41	·5	·40
·3	5·00	·5	·56	·6	·56
·4	·14	·6	·71	·7	·71
·5	·29	·7	·86	·8	·87
·6	·43	·8	13·01	·9	21·03
·7	·57	·9	·16	15·0	·19
·8	·71	10·0	·31	·1	·35
·9	·86	·1	·46	·2	·51
5·0	6·00	·2	·61	·3	·68
·1	·14	·3	·76	·4	·85
·2	·29	·4	·91	·5	22·02
·3	·43	·5	14·06	·6	·18
·4	·57	·6	·21	·7	·35
·5	·71	·7	·37	·8	·52
·6	·86	·8	·52	·9	·69
·7	7·00	·9	·68	16·0	·86
·8	·14				

In performing the titration as above, the experienced operator is guided by the ear as well as by the eye, for the sound produced on shaking serves to indicate how the reaction between the hardening constituents of the water and the soap is progressing, for as this approaches completion the sound becomes softer, and when an excess of soap has been added the agitation is all but noiseless.

In the case of waters requiring more than 16 c.c. of soap solution for the 50 c.c. of water, it is necessary to take a smaller volume of the water and dilute to 50 c.c. with boiled distilled water. The presence of magnesia salts is indicated in the soap test by the formation of a characteristic light curd, and also by the premature formation of a lather, which again disappears on the further addition of soap solution and shaking. If these signs are exhibited, only such a volume of the water should be taken as, when diluted to 50 c.c., requires not more than 7 c.c. of the soap solution; indeed, it is a very good practice to invariably dilute waters so that not more than 7 or 8 c.c. of soap solution are required. In the presence of magnesia salts the results are always less accurate, and, unless great care is exercised, may become wide of the truth.

Permanent hardness is the name given to that which persists after the water has been boiled, that disappearing in this process being known as the 'temporary' hardness. The permanent hardness is most conveniently determined by taking a small flask with a *very short neck* (the Erlenmeyer shape is very suitable), and adding the water to it until a definite weight (*e.g.* 250 grms.) has been made up. The water is then maintained in gentle ebullition for exactly half-an-hour, and, after cooling, the weight is again made up to the original by the addition of boiled distilled water, the soap titration being then performed on a measured portion of this, as described above.

Some analysts prefer to take a given volume of water and restore the volume after boiling, then removing the precipitated carbonates of lime and magnesia by passing through a dry filter.

The *standard of soap solution* is prepared as follows. A cake of Castile soap is scraped with a knife, and 4–5 grms. of the shavings are dissolved in 500 c.c. of a mixture of two vols. of methylated spirit with 1 vol. of distilled water. Filter off the insoluble matter, and dilute the soap solution with half its volume of water. A portion of this solution is then further carefully diluted until 7·8 c.c. are required to form a permanent lather with a mixture of 25 c.c. of the standard calcium chloride solution (prepared by dissolving ·2 grm. of Iceland spar in dilute hydrochloric acid, and, after driving off excess of acid on the water-bath, making up to 1,000 c.c. with distilled water) and 25 c.c. of distilled water.

Poisonous metals. Of these the only ones which are of practical importance in water analysis are lead, zinc, copper, arsenic, and barium. As they are generally present in only very minute proportions, it is necessary to evaporate large volumes (5 litres and upwards) of water in order to obtain gravimetric determinations in the ordinary way; but the following special methods may be generally employed.

For *lead*, take 100 c.c. of the water, acidulate with a few drops of acetic acid, and then about 5 c.c. of a saturated solution of sulphuretted hydrogen. The colour produced is imitated by adding a known quantity of a standard solution of a lead salt to 100 c.c. of distilled water. Even such small proportions as ·03 part Pb per 100,000 should be invariably recorded. (For the standard solution of lead, dissolve ·1831 grm. crystallised normal lead acetate in 1,000 c.c. distilled water; 1 c.c. = ·0001 Pb.)

For *copper*, the same colorimetric method may be employed as for lead, using for comparison a solution of copper sulphate containing ·0001 grm. Cu in 1 c.c. (·3929 grm. crystallised copper sulphate per litre). In the absence of iron a very delicate colorimetric method may be employed, based upon the reaction between copper salts and potassium ferrocyanide, the water being acidulated with hydrochloric acid, whilst in the presence of iron the blue colouration produced by ammonia may be used.

The presence of *zinc* is generally indicated by the gradual formation of a film of carbonate on the surface of the water when the latter is exposed to the air. Some of this film ignited on platinum foil should leave a residue, which is yellow when hot and white on cooling. The quantity of the zinc may be approximately determined, in the absence of other heavy metals, by acidulating 100 c.c. of the water with dilute hydrochloric acid, and then adding a solution of potassium ferrocyanide. The white turbidity produced is then compared with that obtained from a known quantity of a standard solution of a zinc salt (Snyder, B. B. 1878, 939).

Arsenic is best detected and estimated by Marsh's test; 500 c.c. of the water are rendered slightly alkaline with caustic soda or potash free from arsenic, and evaporated to dryness. The residue is extracted with strong hydrochloric acid, and the liquid introduced into a Marsh's apparatus. The gas is passed through a small U-tube containing pumice soaked in solution of lead acetate, and then through a piece of combustion tube constricted in the middle, where it is heated to redness. The passage of gas through the heated tube is continued for an hour, although nearly all the arsenic is liberated in five or ten minutes. The metallic ring formed is compared with a number of standard rings similarly obtained with known quantities of arsenic. A blank experiment must invariably be performed previously, to control the purity of the chemicals employed.

Barium may be detected and determined by concentrating a considerable volume of the water, acidulating with hydrochloric acid, and after filtering, if necessary, adding a solution of calcium sulphate. The barium sulphate precipitated is then collected and weighed in the ordinary manner.

The colorimetric determination of iron, although not a poisonous metal, may be conveniently referred to at this place.

Iron can generally be estimated colorimetrically by means of ferrocyanide or sulphocyanate. Its determination is frequently of importance in waters used for industrial purposes.

In the ferrocyanide method, the water residue is dissolved in hydrochloric acid and diluted to 100 c.c. Of this 10 c.c. are transferred to a 100 c.c. cylinder; add 1 c.c. of strong nitric acid, dilute to the 100 c.c., stir, and then add 1 c.c. of potassium ferrocyanide solution and mix well. The colour produced is compared with that obtained from a standard iron solution, but the same quantity of nitric acid must be present in each case (Sutton, Volum. Analys. 6th ed. 194; *v.* also Carter Bell, S. C. I. 8, 175).

In the sulphocyanate method, two 100 c.c. cylinders are taken, and into each 5 c.c. of dilute hydrochloric acid (1 : 5) and 5 c.c. of dilute nitric acid (1 : 5), together with 15 c.c. of sulphocyanate solution, are poured; then introduce a measured volume of the liquid to be tested into the one cylinder, and after filling up both cylinders to the mark with distilled water, imitate the red colour obtained with the liquid under examination by running in a standard solution of iron from a burette into the other cylinder. In this way one part of iron is said to be recognisable in fifty millions of water (Thompson, C. J. 1885, 493).

Determination of organic matter. A number of processes have been devised for the determination either of the whole or part of the organic substances present in water. Of those which lay claim to discovering the whole of these organic materials, none are entitled to any confidence, whilst even those which attempt to determine a part, or to indirectly obtain a comparative measure of the organic matter, are also open to objections on the score of accuracy. Only those methods more commonly in use by water analysts will be described here.

(1) *Methods depending on the reduction of potassium permanganate.*

(*a*) *Kubel's process.* In this the reduction is effected in acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity and treated with 5 c.c. dilute sulphuric acid (1 : 3), and then with such a quantity of standard dilute permanganate (equivalent to centinormal oxalic acid) that the liquid is of a strong red colour. The mixture is then boiled for ten minutes, and the excess of permanganate added must be such that the colour is not discharged in this operation. 10 c.c. of centinormal oxalic acid are now added, and into the resulting colourless liquid standard permanganate is then run in until a faint red colour is obtained. The amount of oxygen consumed by the organic matter in the water can then be easily calculated.

(*b*) *Schulze's process.* In this the reduction is commenced in an alkaline and completed in an acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity, ·5 c.c. caustic soda solution (1 : 2) are added, as well as 10–15 c.c. of standard dilute permanganate (equivalent to centinormal oxalic acid). The liquid is boiled for ten minutes, allowed to cool to 50 or 60°C. and then 5 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of centinormal oxalic acid are added, the liquid being shaken and gently warmed until the colour has quite disappeared. Then the standard dilute permanganate is run in until a faint red colour, remaining permanent for at least five minutes, is obtained. The oxygen consumed by the organic matter of the water is then easily calculated.

(*c*) *Forchhammer process.* This resembles Kubel's method, inasmuch as the reduction of the permanganate is effected in an acid solution, but the temperature employed, instead of being defined, is the accidental one of the air of the laboratory.

Two flasks are carefully cleaned and into one 250 c.c. of the water, into the other 250 c.c.

of distilled water, are introduced. To each 10 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of standard permanganate (containing ·395 grm. per litre or ·001 grm. available oxygen in 10 c.c.) are added, and the mixture is allowed to stand for three hours. At the end of this time the excess of permanganate remaining is determined by adding two drops of potassium iodide (1 : 10) to each flask, and then running in a standard solution of sodium thiosulphate (1 grm. per litre) until the whole of the free iodine is removed, a drop of clear starch solution being added at the close of the operation. The amount of permanganate destroyed in the blank experiment must of course be deducted from that destroyed in the case of the water, and from the difference the oxygen consumed by the organic matter of the water can be calculated (Tidy, C. J. 1879, 66).

It must be pointed out that in these several methods depending on the reduction of permanganate, the results are only comparative for the same kind of organic matter, a given weight of organic carbon in different kinds of water consuming different quantities of oxygen from permanganate under the same conditions. Thus it has been found that for surface waters, such as those of the rivers Thames and Lea, by multiplying the oxygen consumed in the Forchhammer process by the factor 2·38, the proportion of organic carbon (as determined by combustion) is approximately obtained, whilst in the case of deep well water the factor which must be employed is 5·8 (Woodland Toms).

Again, all these methods are affected by the presence of nitrites, ferrous salts, and larger quantities of ammonia compounds, all of which exercise a reducing action on permanganate. By determining the nitrous acid, a correction can be made for this, whilst the ferrous can generally be converted into ferric iron by shaking up the water several times in a half-filled bottle previously to the oxidation with permanganate; and the error due to ammonium salts is so small that it can generally be neglected (even one part NH_3 per 100,000 has no appreciable reducing effect) (Preusse and Tiemann, B. B. 12, 1906).

(2) *Determination of organic carbon by oxidation of organic matter with potassium dichromate and sulphuric acid* (Wolff, Degener, and Herzfeld). 500–1,000 c.c. of the water are introduced into a capacious retort, the neck of which is drawn out and bent downwards and is connected with a Liebig's condenser. This arrangement enables the retort to be turned upwards and the condenser downwards, thus preventing any loss by spurting during distillation, which is carried on until 250–700 c.c. (according to the volume of water employed) have passed over. The distillate is submitted to Kubel's method (*v. supra*) to ascertain whether any volatile organic matters are present. Alkaline waters should be saturated with carbonic anhydride, and acid waters carefully neutralised with sodium carbonate before the above distillation. The water remaining in the retort is evaporated down to 15 c.c. in a glass dish on a water-bath, the access of dust being carefully avoided. This concentrated liquid is introduced into a flask of 250–300 c.c. capacity, and the dish and retort are rinsed with 10 c.c. of dilute sulphuric acid (1:3), these rinsings being also added to the water in the flask. The decomposition of carbonates caused by the addition of this acid is completed by heating to 50°C. and shaking, and the evolved carbonic anhydride completely displaced by air. After cooling the flask and its contents, 10 grms. of finely-powdered potassium dichromate are added, and the flask is then attached to the remainder of the apparatus. An india-rubber stopper with three holes is placed in the flask; through one hole passes a thermometer dipping into the liquid, through a second passes nearly to the bottom of the flask the tube of a bulb-funnel (A) provided with a stopcock, whilst through the third passes the bent tube of an inverted Liebig's condenser (B). The upper extremity of the condenser (B) is connected with two U-tubes (C and D) filled with fused calcium chloride, whilst between these is a third U-tube (E) containing coarsely-powdered antimony. Of these, C and D are intended to absorb the moisture passing the condenser, and the intermediate one, E, to retain any chlorine. Following on these tubes is a set of weighed potash-bulbs (F) for the absorption of carbonic anhydride, and these bulbs are, of course, protected from ingress of air on the other side by means of a calcium chloride tube, which can be attached to an aspirator at the close of the experiment. The apparatus having been thus put together, 50–60 c.c. of diluted sulphuric acid (3:2) are gradually added through the stoppered funnel (A). During the first half-hour the temperature is kept at 50–55°C., whilst during the second half-hour it is gradually raised to boiling, which is maintained from five to ten minutes. The aspirator is then attached, the air which enters by the funnel (A) having been previously freed from carbonic anhydride by bubbling through caustic potash. The increase in weight of the potash bulbs (F) gives the weight of carbonic anhydride evolved, from which the carbon itself can be easily calculated (B. B. 1886, 2618; Tiemann-Gärtner, Untersuch. d. Wassers, 247).

For a somewhat similar method of determining organic carbon in which permanganate is used instead of dichromate, see Blair, Organic Analysis of Potable Waters, Churchill, 1891, 83. The method appears worthy of more extended trial.

(3) *Determination of organic carbon and nitrogen by combustion.* (*a*) *Frankland and Armstrong's process* (C. J. 6, 77). This method, which is unquestionably the most rational and exact, has been adopted to a comparatively limited extent by water analysts in consequence of the special apparatus and manipulative skill which it entails. The method will be only described in outline here, and for full particulars the reader is referred to Sutton's Volumetric Analysis, E. Frankland's Water Analysis, and P. F. Frankland's Agric. Chem. Analysis, whilst for a critical survey of the methods employed in the organic analysis of water he should not fail to consult Mallet, Report of the United States National Board of Health, 1882.

The process is divisible into three parts: (1) the evaporation of the water, (2) the preparation and combustion of the residue thus obtained, and (3) the measurement of the gases evolved in the combustion.

For the *evaporation*, from 100 c.c. (in the case of sewage and highly-polluted waters) to 1,000 c.c. (in the case of very pure waters) are measured into a clean flask, 20 c.c. of a saturated solution of sulphurous acid being added together with a drop of a solution of ferric chloride; the liquid is then rapidly boiled for a few seconds. This treatment secures the decomposition of carbonates, nitrates, and nitrites, whilst any ammonia is fixed by the sulphurous acid, and this ammoniacal nitrogen, which has been previously determined, must be deducted from the total amount of nitrogen obtained in the combustion. The water is now rapidly cooled, and the evaporation commenced in an apparatus specially designed for the purpose. This consists of a nearly hemispherical glass dish about 4 inches in diameter and without a lip. It is floated in a shallow copper basin heated below by a water-bath provided with constant feed, and on the flange of this copper basin there rests a truncated conical ring, constructed of lead or copper, and about 3 inches in height, whilst upon a flange at the top of this again rests a tall glass shade about 12-18 inches in height. The water for evaporation is placed in a flask which is provided with a delivery tube of special construction ground on to its neck, and which serves, when the flask is turned upside down, to maintain the water at a constant level in the glass dish in which the evaporation is proceeding, for this delivery tube is made to pass through a notch in the truncated conical metal ring, just beneath the glass shade which the the latter supports, and delivers into the centre of the glass dish within. In the writer's laboratory, the evaporation of 500 c.c. of water is found to take from 10-12 hours. The evaporation should be continued until the residue is quite dry, and if the water contains only a small amount of total solids it is advisable to add a little ignited calcium phosphate to the dish before commencing the evaporation. In the analysis of sewage, or waters containing much ammonia and *no nitrates or nitrites*, it is advantageous to use 10 c.c. of a solution of metaphosphoric acid (1:10) instead of the sulphurous acid, as ammonium phosphate loses much less ammonia during evaporation than ammonium sulphite. A little ignited calcium phosphate should also be added to dry the residue in this case. But if there are no nitrates and nitrites and much ammonia, the more satisfactory, although more laborious, plan is to use a little ignited borax instead of the sulphurous or metaphosphoric acid. In this way the ammonia is completely dissipated on evaporation, and as no correction has, therefore, to be applied to the organic nitrogen found, the result is more correct. But as boric acid does not entirely decompose carbonates the accuracy of the organic carbon found by this method may be seriously affected, and it is advisable to make a separate determination of the carbon in a second experiment in which the sulphurous acid method is employed. Unless this method be adopted the results for organic nitrogen in the presence of much ammonia are nearly sure to be highly inaccurate.

If the water contains more than ·5 part per 100,000 of nitrogen as nitrates and nitrites, the 20 c.c. of sulphurous acid employed above may not improbably prove insufficient for their complete destruction, and in the case of such waters the residue in the dish should be further treated with 10 c.c. of sulphurous acid, this evaporated off, and if the amount of nitric or nitrous nitrogen exceed 1 part per 100,000 this treatment of the residue with further quantities of sulphurous acid may be repeated twice or three times to secure complete destruction of the nitrates and nitrites.

The *preparation and combustion of the residue* thus obtained is effected by thoroughly mixing with the latter in the dish a small quantity of finely divided and carefully ignited copper oxide. This is then completely transferred to a narrow piece of combustion tubing about 18 inches long and sealed at one extremity. The dish is again rinsed with a little fine oxide, and this also transferred to the tube. Coarse and carefully ignited oxide of copper (preferably from wire) is then introduced to a depth of about 10 inches, whilst the fine oxide previously introduced will occupy about 2 inches. Upon the stratum of coarse oxide follows a copper gauze cylinder 3 inches in length, and then another layer of coarse oxide about 1 inch long. The open extremity of the tube is now drawn out over the blowpipe, so that it can be connected with a Sprengel mercury pump. The tube is completely exhausted, and the combustion performed *in vacuo* in the ordinary way, the evolved gases being then drawn over by the pump and collected in a test tube filled with mercury and placed over the lower open extremity of the fall tube in the trough below.

The *volumetric measurement of the gases* (consisting of carbonic anhydride, nitrogen, and possibly also nitric oxide and sulphurous anhydride) collected as above is carried out in the Frankland gas apparatus, which admits of the measurement of very minute quantities of gas. Three measurements only are necessary. In the first place the gas is treated with a few drops of a saturated solution of potassium dichromate to absorb any sulphurous anhydride that may be present. The volume of the gas is then accurately measured, after which it is treated with a few drops of strong caustic potash, which rapidly removes the carbonic anhydride, after which the volume of the remaining gas is again carefully ascertained. The residual gas now consists of nitrogen, with possibly a little nitric oxide. It is mixed with a bubble of pure oxygen in order to convert any nitric oxide into nitrous and nitric acids, which are immediately absorbed by the caustic potash present, and then, on adding a drop or two of solution of pyrogallic acid, the excess of oxygen is absorbed and the remaining gas, which consists of nitrogen, is carefully measured. The diminution in volume effected by the caustic potash in the first instance obviously represents the carbonic anhydride, whilst the final volume of residual gas, together with one-half of the contraction resulting from the addition of oxygen and pyrogallic acid, represent the total volume of nitrogen. From these volumes the weights of carbon and nitrogen respectively can be easily calculated. As already pointed out, if sulphurous or metaphosphoric acid has been used in the evaporation, and ammonia is present in the water, the ammoniacal nitrogen (subject to an empirical correction for loss of ammonia during evaporation) has to be subtracted from the total nitrogen found by combustion. A small correction (ascertained by blank experiments made from time to time with the reagents employed in the evaporation and combustion) has also to be applied to the carbon and nitrogen thus determined.

For *Dupré and Hake's method*, in which the organic carbon is determined by the combustion of the water residue with oxide of copper in a stream of oxygen, the carbonic anhydride being absorbed by baryta water, and the barium carbonate either weighed or estimated by the degree of turbidity occasioned in the solution of baryta—the organic nitrogen is not determined—see C. J. 1879, 159.

Dittmar and Robinson's method of determining organic carbon is essentially similar to Dupré and Hake's. The gases proceeding from the combustion tube are, however, first passed through a U-tube containing a solution of chromic acid in 60 p.c. sulphuric acid to absorb moisture and sulphurous acid (the water is evaporated with sulphurous acid for the preparation of the residue), the carbonic anhydride being then absorbed in a weighed soda-lime tube (C. N. 1877, vol. 36, 26). A method of determining organic nitrogen has also been devised by Dittmar and Robinson, and is described below.

(4) *Methods for determination of organic nitrogen only.* Of these the most common one in use is the well-known

(*a*) '*Albuminoid ammonia*' *process* of Wanklyn, Chapman, and Smith (C. J. 1867, 591), which does not yield the whole, but only very variable proportions, of the organic nitrogen in different nitrogenous organic substances, although in the case of some—such as leucine, aspartic acid, tyrosine, &c.—which frequently appear as decomposition products of albuminous matters, nearly the whole of the nitrogen is obtained as ammonia (Preusse and Tiemann, B. B. 12, 1906; Mallet, U. S. National Board of Health Report, 1882). As this method thus affords a means of distinguishing between different kinds of organic substances, it should not be neglected by water analysts, although it is highly undesirable to limit the determination of organic matter, as is so frequently done, to the results obtained by this process.

The method has already been described in p. 981.

(*b*) *Dittmar and Robinson's process.* In this process the residue, obtained in just the same way as for the combustion process, is heated with fused caustic soda, or soda and baryta, in a copper or silver boat placed in a combustion tube in a current of hydrogen, the evolved ammonia being absorbed by very dilute hydrochloric acid, which is subsequently Nesslerised. (C. N. 1877, 36, 26). The results are accurate, and coincide with those obtained by the combustion process of Frankland and Armstrong.

(*c*) *Kjeldahl's process.* This well-known and recently much-employed method for determining organic nitrogen has been adapted for use in water analysis by Drown and Martin (C. N. 59, 272). The method appears to give accurate results which are uninfluenced by the presence of nitrates and nitrites in such quantities as are found in ordinary waters. 500 c.c. of the water are placed in a round-bottomed flask of about 900 c.c. capacity; the volume is then reduced to about 200 c.c. by boiling, and to this, after cooling, add 10 c.c. of pure concentrated sulphuric acid. The mixture is then cautiously boiled, with the flask in an inclined position, until all the water has been driven off and the acid remains of a white or very pale-yellow colour. After removing the source of heat, add a little powdered permanganate until, on shaking, the liquid becomes green, showing that excess has been added. If a purple instead of a green colour appears, it shows that the whole of the water has not been driven off. When cool, 200 c.c. of water free from ammonia are added, care being taken to rinse round the neck of the flask, and thus wash in any acid which may be adhering there. 100 c.c. of sodium hydrate solution are then added, and the mixture distilled with a Liebig's condenser. (The sodium hydrate solution is prepared by dissolving 200 grms. of good caustic soda in 1,250 c.c. of distilled water, adding 2 grms. potassium permanganate, and boiling down until the volume is rather less than 1,000 c.c., making up to 1,000 c.c. when cold.) The distillate is collected in a flask containing 50 c.c. of water free from ammonia, and 1 c.c. of dilute pure hydrochloric acid, and during the distillation of the first 50 c.c. the delivery tube of the condenser is made to dip into this acid liquid, whilst during the remainder of the distillation the flask is lowered so that the delivery tube is just above the liquid. The distillation is carried on until the whole of the ammonia has passed over, and the contents of the receiver are then Nesslerised in the ordinary way. The most scrupulous care must be exercised to prevent access of ammonia from the air and regaents; a blank experiment should also be made for control (Sutton, Volum. Analys. 6th ed. 434).

Determination of dissolved oxygen. Much importance is, with very little reason, attributed by some analysts to this determination; it can, moreover, be rarely applied, as the samples must be collected with special precautions if the results are to have any value at all. The various processes in use have recently been examined by Kisch (C. J. Abst. 1892, 98). *Reichardt's* method (Zeitsch. f. Analyt. Chem. 11, 1872, 271), as modified by Preusse and Tiemann (B. B. 12, 1879, 1768; Tiemann-Gärtner's Untersuch. d. Wassers, 278) has been found both simple and effective in the laboratory of the writer. It consists in boiling a measured volume of water, and collecting the gases over a hot solution of caustic potash, the oxygen being then estimated either by explosion with hydrogen, or by absorption with potassium pyrogallate. In *Mohr's* method (Mohr's Titrirmethoden) the sample is mixed with an acid solution of ferrous sulphate of known strength, then with caustic soda to throw down the ferrous hydrate, and after remaining for a few hours (air, of course, being rigidly excluded), the precipitate is re-dissolved in sulphuric acid, and the remaining ferrous sulphate titrated with permanganate. In the *Schützenberger-Risler* process (Bl. 1873, 19, 152; 20, 115; Tiemann-Gärtner's Untersuch. d. Wassers, 277, 288; Catherine Williams and Ramsay, C. J. 1886, 760; Bernthsen, B. B. 13, 2277; Roscoe and Lunt, C. J. 1889, 552; Dupré, An. 1885, 10, 156) the water is allowed to act on a solution of sodium hydrindigotin disulphonate, which is thereby converted into the blue compound, a standard solution of sodium hyposulphite being then run in until the liquid is again colourless. In *Winkler's* process (B. B. 21, 2843) the water is mixed with a solution of manganous chloride, and then with potassium iodide and caustic potash; the precipitated manganous hydrate absorbs the oxygen, passing into a higher state of oxidation. On then adding hydrochloric acid the higher oxide of manganese gives rise to the liberation of an equivalent quantity of iodine, the amount of which is determined by titration with sodium thiosulphate. According to Kisch (*l.c.*), the results by the Reichardt-Preusse-Tiemann method are decidedly lower than those obtained by the Winkler process, which is in harmony with the experience of the writer. The results by Mohr's and Schützenberger's methods accord very well with those by Winkler; but Winkler's appears, on the whole, to be the most trustworthy, and the easiest to carry out. For Thresh's method, *v.* C. J. 1890, 185.

Determination of carbonic acid. (1) The *total carbonic acid* is determined by completely precipitating as calcium carbonate with an excess of calcium hydrate (a sufficient quantity of calcium chloride being added to decompose alkaline carbonates), then filtering off the precipitate, and determining the carbonic anhydride in it in the usual way (Fresenius, Quant. An.; Tiemann-Gärtner, Die Untersuch. d. Wassers, 213). If the water is saturated with carbonic anhydride under pressure, the above method must be preceded by Rochleder's process for estimating the carbonic anhydride which escapes on reducing the pressure to that of the atmosphere (Fr. 1, 20; Sutton's Volum. An. 6th ed. 94).

(2) The *free and semi-combined carbonic acid* is determined by Pettenkofer's method, in which the water is treated with an excess of standard calcium hydrate solution, and, after the precipitate has separated in a *crystalline* form, the clear liquid is decanted off, and the excess of lime ascertained in an aliquot part by titration with standard dilute oxalic acid, using litmus paper as indicator. If the water contains alkaline carbonates, sufficient neutral calcium chloride solution must be added to decompose them, whilst if there is a considerable proportion of magnesia salts, some ammonium chloride must also be added (*v.* Sutton's Volum. An. 6th ed. 94; and Tiemann-Gärtner's Untersuch. d. Wassers, 219–223).

If the carbonic acid thus determined is subtracted from the total obtained according to (1), then the difference represents the combined carbonic acid. To this combined carbonic acid there corresponds, of course, an equal quantity of semi-combined, so that only any excess over and above this can be regarded as free carbonic acid. It must, however, be pointed out that the determination of total carbonic acid generally yields results which are below the truth by 1–1·5 units in 100,000 parts, in consequence of the solubility of normal calcium carbonate itself.

Determination of sulphuretted hydrogen. Colorimetrically with a solution of sodium nitroprusside, using for comparison a standard solution of sulphuretted hydrogen. The latter is standardised by taking a measured volume and adding an excess of decinormal sodium arsenite; shake well, and then acidulate with hydrochloric acid. After the arsenious sulphide has completely subsided, dilute to 300 c.c., and filter through dry paper. Take 100 c.c. of the filtrate, remove acidity by means of solid sodium carbonate, add a drop of starch solution, and then run in decinormal iodine until a blue colour is obtained. This method may, of course, also be employed for the determination of the sulphuretted hydrogen in the water itself if present in sufficient quantity.

In using the colorimetric method, 300 c.c. of the water are treated with 5 c.c. sodium carbonate and 3 c.c. sodium hydrate; allow the precipitate to subside for 1–2 hours, then decant or filter. To 250 c.c. of the filtrate in a colourless cylinder add 1 c.c. of sodium nitroprusside solution (4 grms. per litre), and for comparison take 245 c.c. distilled water, to which add 2 c.c. sodium hydrate and as much of the standard solution of sulphuretted hydrogen as is required to produce precisely the same tint as is obtained with the water above. In this manner ·1 part SH_2 per 100,000 can be determined (Tiemann-Gärtner, Untersuch. d. Wassers, 232).

Sulphuretted hydrogen may also be accurately determined by means of centinormal iodine solution. 10 c.c. or other suitable volume of the latter are placed in a 500 c.c. flask, and the water added until the colour completely disappears; 5 c.c. of starch solution are then added, and centinormal iodine is run in until a blue colour is obtained, pure distilled water being added up to the 500 c.c. mark from a burette. On subtracting the sum of the volumes of iodine, starch solution, and distilled water added from 500 c.c., the volume of water which reacted with the iodine solution employed is ascertained. A correction should be made for the volume of iodine solution required to produce a blue colour (Sutton, Volum. An. 6th ed. 316).

BACTERIOLOGY OF WATER.

The great progress which has been made within recent years in our knowledge of infectious diseases, and of the processes dependent on bacterial life, renders it imperative that the subject of water supply should be considered from a bacteriological, as well as a chemical, point of view. For a general account of micro-organisms and their functions, the reader is referred to the article on FERMENTATION and the various sources of information there referred to. In this place we shall confine our attention to the relationship of bacteria to water, more especially in connection with the communication of zymotic disease.

For some of the first systematic investigations concerning the plants found in water, see Cohn (Beiträge zur Biologie der Pflanzen, 1, 113), Hirt (Zeitsch. f. Biologie, 15, 91), Chamberlain ('Organic Impurities in Drinking Water,' Annual Report of the State Board of Health of Connecticut, 1883), Roth and Lex (Handbuch der Militär-Gesundheitspflege, 1).

On the communicability of diseases through living organisms, see Sievers (Schmarotzerstatistik aus den Sectionsbefunden d. Patholog. Institutes Kiel, 1877–87), Leuckart (Die menschlichen Parasiten,' &c., 1876), Manson (The Filaria Sanguinis Hominis, London, 1883; Lancet, 1887, 713), Leichtenstern (Deutsche med. Wochensch. July, 1885). All the above refer to the introduction of animal parasites through water. Concerning the communication of dysentery through water, see Hirsch (Handb. d. historisch-geograph. Pathologie, 2nd ed. pt. iii. 1886), Kartulis (Zur Aetiologie d. Dysenterie in Aegypten, Virchow's Archiv, 1887, 521).

On the communication of Asiatic cholera through drinking water the most important evidence was adduced by Snow (On the Mode of Communication of Cholera, London, 1855), Farr (Report on the Cholera Epidemic of 1886), Macnamara (A History of Asiatic Cholera, London, 1876). On this subject see also 6th Report of the Rivers Commission, 1874, and 'The Upper Thames as a Source of Water Supply,' Society of Arts Journ. 1884, P. F. Frankland. The exciting cause of cholera is believed by many to be the *spirillum choleræ Asiaticæ* discovered by Koch, and found by him, amongst other places, in the tank water of Calcutta (Bericht über die Thätigkeit der zur Erforschung der Cholera im Jahre 1883 entsandten Commission, Berlin, 1887, 182); also by Nicati and Rietsch, in the water of the harbour of Marseilles (Revue d'Hygiène, 1885).

The other zymotic disease which has been most conclusively proved to be communicable by drinking water is typhoid fever (Thorne Thorne at Caterham, 6th Report of Rivers Commission, 167, 179; Zuckschwerdt, Publicationen d. Vereins f. öffentliche Gesundheitspflege in Halle, iv.). The exciting cause of this disease is generally believed to be a bacillus, discovered by Eberth-Gaffky (Eberth, Der Typhusbacillus und die intestinelle Infection,' Volkmann's klin. Vorträge, 1883; Archiv f. pathol. Anatomie, 81, 1880; 83, 1881; Gaffky, Mittheil. a. d. kais. Gesundheitsamte, 2, 1884), and which has, on a number of occasions, been actually found in water suspected of giving rise to typhoid. Moers (Ergänzunsheft Centralbl. f. allgem. Gesundheitspflege, 2, 1886, 144; Schilling's Journ. f. Gasbeleucht. und Wasserversorg. 1887), Michael (Typhusbacillen im Trinkwasser, Fortschritte d. Medicin, 4, 1886, 353), Dreyfus-Brisac and Widal (Épidémie de Famille de Fièvre Typhoïde. Considérations Cliniques et Recherches Bactériologiques,' Gaz. Hebdom. 1886, No. 45), Chantemesse and Vidal (Enquête sur une Épidémie de Fièvre Typhoïde à Pierrefonds, 1886, Rev. d'Hygiène, 9, 116; Archiv. de Physiol. et Pathol. 1887, 217), Brouardel and Chantemesse (Enquête sur les Causes de l'Epidémie de Fièvre Typhoïde à Clermont-Ferrand, Rev. d'Hygiène, 9, 368), Beumer (Zur Aetiologie d. Abdominal-Typhus, Deutsche Med. Wochensch. 1887, No. 28); to which might be added the results of other observers (Trans. of the Internat. Congress of Hygiene, London, 1891).

As it is only under the most exceptional circumstances that the discovery of such pathogenic forms can be expected, the bacteriological examination of water is generally restricted to a determination of the number of microbes present in water. Even this investigation is attended with insuperable difficulties, in consequence of the impossibility of obtaining a culture-medium suitable for all kinds of bacteria, and hence only comparative results can be secured by using one and the same culture material for different waters. The material which has come into practically universal use for this purpose is Koch's gelatin-peptone. (For the preparation of this material and the method of employing it in plate-cultures for the numerical determination and isolation of micro-organisms, see FERMENTATION, vol. ii. 114, 115.) In the case of waters containing comparatively few microbes 1 c.c. or ·5 c.c. is employed for the plate cultivation; but if a large number are present it is necessary to suitably dilute the sample with sterilised distilled water before submitting it to plate culture. In all cases the sample should be violently agitated, so as to secure a uniform distribution of the microbes before taking out the measured quantity for cultivation. The water for examination must be collected in sterilised flasks, plugged with sterile cotton-wool; or, if they have to travel some distance, it is preferable to collect them in small, accurately stoppered bottles, previously sterilised, and contained in small sterile tin canisters. In all cases, the plate cultures must be made as soon as possible after collection (within a few hours), as otherwise more or less extensive multiplication of the microbes may have taken place, and during any unavoidable interval the samples should be kept in a cool place, preferably in a refrigerator.

Number of micro-organisms in different waters. Since the introduction of Koch's method of gelatin-plate culture, referred to above, a very large number of waters have been submitted by its means to quantitative examination for micro-organisms. It was at first believed that the number of microbes present in a given volume of water would give a useful indication as to its purity or otherwise, and artificial standards were set up, according to which waters were classified as of good, medium, or bad quality, according to the number of microbes found by the gelatin method in 1 c.c. It was, in fact, not unnaturally supposed that in waters containing a large number of microbes there would be more chance of dangerous forms being present than in those containing a small number only. This view, which was never advocated by the writer, has had to be greatly modified or entirely abandoned, from the fact, which has been abundantly established, that many bacteria are capable of enormous and extraordinarily rapid multiplication even in waters of very high organic purity. Indeed, the rate of multiplication is often greater in a pure than in a contaminated water (P. F. Frankland, On the Multiplication of Micro-organisms, Pr. 1886, 526; Wollfhügel and Riedel, Arbeiten a. d. k. Gesundheitsamte, 1, 455; Meade Bolton, Zeitsch. f. Hygiene, 1, 76; Leone, G. 15, 385).

On this account many of the statements which have been made concerning the number of micro-organisms in water must be accepted with reserve, as, unless the samples have been examined within a very short time (a few hours) after collection, the numbers found may bear no sort of relationship to those actually present at the moment of collection. Moreover, on account of this multiplication it is obvious that the quantitative determination of microbes in natural waters has generally but little interest, as the number found must so largely depend upon the extent to which such multiplication may have taken place previous to collection. On the other hand, the determination is invaluable for ascertaining the effect of methods of water purification, either natural or artificial, in the removal of micro-organisms (P. F. Frankland, The Removal of Micro-organisms from Water, Pr. 1885; S. C. I. 1885 and 1887; Salamon and Mathew, S. C. I. 1886, 261).

In applying the bacteriological method to this purpose, however, it is necessary that the water should be submitted to examination *immediately* after having undergone the purification process, otherwise the results may be altogether disturbed through subsequent multiplication. Reference has already been made to the removal of micro-organisms by filtration and other methods of water purification on pp. 971–975.

After the above introductory remarks, the table on the next page will sufficiently speak for itself, illustrating as it does the number of microbes found in natural waters of different kinds, and also the effects of various processes of water purification as regards their removal.

Behaviour of pathogenic micro-organisms in water. Inasmuch as it is only under very exceptional circumstances that pathogenic microbes can be actually discovered in water, we have to draw most of our inferences concerning their behaviour in water, partly from the behaviour of the ordinary microbes which we find in natural waters, and partly from the behaviour of pathogenic forms which are intentionally introduced into water for experimental purposes. Thus, in investigating processes for the purification of water, we may form just as valuable, or even a more valuable, judgment from the effect of a process on the ordinary bacteria found in water than if we had employed for experiment some particular pathogenic form. For instance, if it be found that some process of filtration removes 90 p.c. of the varied collection of bacteria present in river water, this result will be of greater value in forming an average estimate of the efficiency of this filtration process than if the experiment had been made on some single form known to possess pathogenic properties. On the other hand, inasmuch as many pathogenic forms are probably not by nature inhabitants of water at all, it becomes of great interest and sanitary importance to ascertain whether, and to what extent, such pathogenic forms are capable of preserving their vitality in this medium. A great number of experiments have been made in this direction during the past seven years, the vitality of many known pathogenic forms having been tested in waters of different kinds. From these experiments it appears that but few pathogenic forms are capable of extensive multiplication in ordinary potable water, although some multiply abundantly in sewage. Some forms, again, are very rapidly destroyed, even in a few hours, by immersion in water, whilst others are much more hardy; and those which form spores can be preserved in that state for days, weeks, months, or practically an indefinite period of time. In most of these experiments the artificial condition has been preserved of introducing the pathogenic form into sterilised water, whilst in comparatively few only has water in its natural state and with its contained bacteria been used. The results obtained in the latter case must be accepted with considerable caution in consequence of the great difficulty of discovering a few pathogenic forms amongst a vast number of the ordinary water bacteria. The general tendency of the results, however, is unquestionably to show, as might indeed be anticipated, that in the presence of numerous competitors, in the shape of the ordinary water bacteria, the vitality of the pathogenic forms is considerably reduced.

The question of the vitality of micro-organisms is of such manifest importance, and so variable in different species and under different conditions of medium, temperature, &c., that a large amount of work still remains to be done in this direction. Even the spores of different microbes are subject to great variations in their vitality. Thus whilst the spores of the tuberculosis and typhoid bacilli, on being dried at the ordinary temperature, remain alive only for a few months, those of anthrax can retain their virulence for upwards of fifteen years (Koch, I. Cholera-conference), and some forms of bacteria have been found alive after remaining twenty-five years in a liquid medium (Duclaux, C. R. 1885).

In the case of *anthrax*, it has been shown that the bacilli perish when kept in sterilised water within a few days, although the precise period is subject to considerable variations, whilst the spores retain their vitality for practically an indefinite length of time; and the writer has also found that, in sterilised sewage, the anthrax bacilli can undergo very considerable multiplication (Wolffhügel and Riedel, Arbeiten a. d. kaiserl. Gesundheitsamte, 1886; Meade Bolton, Ueber das Verhalten verschiedener Bacterien im Trinkwasser, Zeitsch. f. Hygiene, 1; P. F. Frankland, S. C. I. 1887).

In unsterilised water Kraus (Archiv f. Hygiene, 6, 234) found that sporeless anthrax bacilli lost their vitality in from two to four days. *V.* also Uffelmann (Trinkwasser und Infektionskrankheiten, Centralbl. f. Bakteriologie, 5, 89) and Karlinski (Ueber das Verhalten einiger pathog. Bakterien im Trinkwasser, Centralbl. f. Bakt. 6, 138 and 671). De Giaxa (Centralbl. f. Bakt. 6, 497) has studied the disappearance of anthrax and typhoid bacilli in sea water. Hochstetter (Ueber Mikroorganismen im künstlichen Selterswasser, Arbeiten a. d. kaiserl. Gesundheitsamte, 2), Hüppe (Hygienische Beurtheilung d. Trinkwassers vom biolog. Standpunkte, Journ. f. Gasbeleucht und Wasserversorg, 1887).

As regards the vitality of the *cholera spirilla* (Koch) in water, very divergent results have been obtained even by one and the same observer. The probable explanation of these discrepancies has been given by the writer, who has

Number of Micro-organisms in Water.

Description of water	Number of developable micro-organisms obtained from 1 c.c. of water	Authority
River water.		
Thames at Hampton (average for 1886) .	20,255	P. F. Frankland (S. C. I.)
Lea at Chingford (average for 1886) . .	19,781	,, ,, ,,
Thames, filtered by London companies (average for 1886)	402	,, ,, ,,
Lea, filtered by East London Company (average for 1886)	253	,, ,, ,,
Spree above Berlin (Sept. 29, 1885) . .	1,120	Plagge and Proskauer (Zeitsch. f. Hygiene, 2, 401)
Ditto after sand filtration (Sept. 29, 1885)	30	,, ,, ,,
Spree above Berlin (Nov. 24, 1885) . .	31,500	,, ,, ,,
Ditto after sand filtration (Nov. 24, 1885)	167	,, ,, ,,
Spree within Berlin (August 8, 1886) .	144,000	Frank (Zeitsch. f. Hygiene, 3, 355)
,, ,, ,, ...	136,000	,, ,, ,,
,, ,, ,, ...	385,000	,, ,, ,,
,, ,, ,, ...	540,000	,, ,, ,,
Rhine at Mühlheim (June 3, 1885) . .	21,000	Moers (Tiemann-Gärtner's Untersuch. d. Wassers, 443
Main, above Würzburg (Feb. 1886) . .	520–1,020	Rosenberg (Archiv f. Hygiene, 1886, 448)
Main, below ,, ,, . .	2,950–22,000	,, ,, ,,
Inland lakes.		
Lake of Zürich (average for 1884–5). .	168	Cramer (Wasserversorgung v. Zürich)
Lake of Lucerne (1884)	8–51	,, ,, ,,
Lake of Geneva (1884)	38	Fol and Dunant (Recherches sur le Nombre des Germes Vivants que Renferment quelques Eaux de Genève)
,, ,, (near the shore) . .	150,000	
Deep wells.		
London (Kent Company's) wells at Deptford, 1885	6–8	P. F. Frankland (S. C. I. 1885)
Ditto, 1886	4–82	,, ,, ,, 1886
Well at Bushey (Colne Valley) . .	322[1]	,, ,,
Ditto, after softening by Clark's process .	4	,, ,,
Well at Victoria Dock (London) . .	182[1]	,, ,,
Ditto, after softening by Gaillet and Huet's process	4	,, ,,
Vienna deep-well water	18–33	Kowalsky
Mayence, artesian well	4	Egger
Wiesbaden, deep well at slaughterhouse .	4	Hüppe
Springs.		
Reigate spring, Upper Greensand (1885) .	8	P. F. Frankland (*l.c.*)
Jena, springs near	32–156	Fürbringer (Arbeiten a. d. k. Gesundheitsamte, 2)
Frankfurt, spring water supply . . .	0–60	
Danzig, spring water supply . . .	0–2	Libbertz ,, ,,
Brunnthal spring	4–35	Freimuth ,, ,,
Giesing spring	0–5	Buchner ,, ,,
Leitmeritz, springs in town . . .	700–3,000	Maschek
Sea water.		
Gulf of Naples, samples taken from depths of 75–800 mètres, at distances of 4–15 kilos. from shore	6–78	Russell (Untersuchungen über im Golf v. Neapel lebenden Bacterien, Zeitsch. f. Hygiene, 11 (1891), 177)
Ditto, 50 mètres from entry of Chiatamone Canal	298,000	De Giaxa (Zeitsch. f. Hygiene, 6 (1889), 186)
Ditto, 350 mètres from entry . . .	26,000	,, ,, ,,
Ditto, 3 kilos. from entry	10	,, ,, ,,

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[1] This sample was not taken directly from the well, but serves to show the effect of Clark's process.

found that if the spirilla are taken from old and weakened cultures and introduced into sterile water their vitality is rapidly lost, whilst if the same weakened spirilla are first revivified by cultivation in broth, and are then introduced into the same water, their vitality is retained for a much longer period of time. The cholera spirilla may, indeed, undergo a slight multiplication in sterile potable water, whilst in sterile sewage their numbers increase enormously (P. F. Frankland, The Multiplication of Micro-organisms, Pr. 1886, 40, 541; S. C. I. 1887, 320). In the sterilised water of the Berlin supply, Hochstetter (Untersuch. d. Wassers, Tiemann-Gärtner, 595) found the cholera spirilla still alive after 392 days. It has also been found by Gruber (Wiener Med. Wochensch. 1887, Nos. 7 and 8) that the cholera spirilla can multiply in the presence of the bacteria of putrefaction. *V.* also Nicati and Rietsch (Rev. d'Hygiène, 1885, No. 5), Koch (Berl. Klin. Wochensch. 1885, No. 37, *a* and *b*); Babes (Untersuchungen üb. Koch's Kommabacillus, Virchow's Archiv, 99), Wolffhügel and Riedel (Arbeiten a. d. k. Gesundheitsamte, 1886).

With the *typhoid bacilli* (Eberth-Gaffky) numerous experiments have also been made. These have shown that in sterilised potable water the bacilli can undergo considerable multiplication at ordinary temperatures, and have sometimes been found alive after remaining for three months in such water at the ordinary temperature of the air, although in many cases they disappear much more rapidly. On the other hand, when the bacilli are introduced into unsterilised water their disappearance is more rapid than in the sterile water, but they have sometimes been discoverable as long as thirty days after introduction, in spite of the abundant multiplication of the water bacteria simultaneously present (Wolffhügel and Riedel, Meade Bolton, Hochstetter, Krauss, Hüppe, Chantemesse and Widal; for references see above). *V.* also Heræus (Zeitsch. f. Hygiene, 1, 233), and Seitz (Bakter. Studien zur Typhusätiologie, Munich, 1887, p. 33). The typhoid bacilli have also been found to retain their vitality in ice which had remained frozen for upwards of 100 days (Prudden, Centralbl. f. Bakteriologie, 1, 650; P. F. Frankland, The Hygiene of Water Supply, Nature, 45, 1891, 25).

Of other pathogenic microbes which have been similarly experimented with, the *streptococcus of erysipelas* (Fehleisen) was found to lose its vitality with great rapidity in sterile potable water, and even in sterile sewage it was no longer demonstrable after five days (P. F. Frankland, S. C. I. 1887, 319). Similarly, the *micrococcus tetragenus* disappeared in about four days, whilst the *staphylococcus pyogenes aureus* was more permanent, being in some cases still demonstrable after twenty to thirty days' residence in sterilised well water (Meade Bolton, Zeitsch. f. Hyg. 1, 106, 1886).

The *bacillus pyocyaneus*, again, was found to undergo multiplication even in sterile distilled water, as well as in potable waters and sewage (P. F. Frankland, The Multiplication of Micro-organisms, Pr. 1886, 537).

Specific micro-organisms found in water. Since the introduction of Koch's methods of culture on solid media, the identification of particular bacterial forms has become more possible, as the microscopic characters of an organism can be generally supplemented by invaluable naked-eye appearances to which it may give rise when grown on different media. A number of different forms derived from water have been isolated by various observers, and their characters more or less fully described. Even when such particulars are given, it is often a matter of great difficulty to identify forms, as the characteristics are not unfrequently subject to more or less considerable variation in consequence of the particular conditions to which an organism may have been subjected during previous generations, such variations often persisting for a number of generations, if not indefinitely. It is impossible in this article to give a description of the various forms which have been isolated from water, for which the reader is referred to the following sources:—

Bakteriologische Diagnostik; Eisenberg, Leipzig.

Die Mikroorganismen; Flügge, Leipzig.

Ueber das Verhalten verschiedener Bakterienarten im Trinkwasser; Meade Bolton, Zeitsch. f. Hygiene, 1, 76.

Ueber einige typische Mikroorganismen im Wasser und im Boden; Grace C. Frankland and P. F. Frankland, Zeitsch. f. Hygiene, 6, 373.

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WATERS, AERATED, *v.* Aerated waters.

WATER STONES *v.* Agate.

WAXES. The waxes are a group of substances of animal or vegetable origin, resembling beeswax in their physical properties, and composed of the elements carbon, hydrogen, and oxygen. Solid paraffin is sometimes called a wax, as physically it resembles beeswax, but it is not of immediate animal or vegetable origin, and it does not contain oxygen, so it is most conveniently excluded from this group. The waxes are mixtures and not single chemical substances, and among their proximate constituents are included a considerable portion either of some free fatty acid or of esters containing some radicle other than glyceryl $(C_3H_5)'''$; some of them also contain a proportion of glyceryl esters, and others are free from these. Physically, the waxes come in the series: (1) fixed animal and vegetable oils; (2) soft fats; (3) tallow-like bodies and solid fats; (4) waxes proper; and (5) resins.

Below is given a description of those animal and vegetable waxes which are of industrial importance, but besides these waxes occur in many plants in small proportions (*cf.* Oils, fixed, and fats).

Balanophore wax is derived from the parenchymatous cells of *Langsdorffia hypogæa* (Mart.), a native of Brazil, and of *Balanophora species*, a native of Java and the neighbouring islands; which are parasitic plants some 5 or 6 cm. long, growing on the roots of other plants. These plants are so rich in wax that they can be set on fire and burn with a luminous flame, and torches can be made by coating wooden sticks with the plant made into a paste.

By boiling the plant the wax is procured as a greyish or yellowish mass. Ether extracts it from the plant, and as thus obtained it has the colour and consistence of natural beeswax; it melts at about 100°, has a specific gravity at 15° of 0·995, and is easily soluble in ether, and only very sparingly soluble in alcohol. The wax has the property of dissolving in cold sulphuric acid and being reprecipitated by water. It is a resinous wax, and also contains a glyceride.

Beeswax, *Cera*, is produced by the common bee, *Apis mellifica* (Linn.), and also by some allied species, for instance, *Apis fasciata*, in South America, and *Apis unicolor* in Madagascar. *Andaquies wax* is obtained from a species found near the Orinoco and Amazon rivers. Beeswax is not collected from the flowers by the bee, but is the secretion of certain organs situated beneath the rings of the abdomen of the neuter or working bees, and is used by them in forming the cells of the honeycomb. The comb yields approximately ten times more honey than wax.

The honey is allowed to run out from the comb, which is then pressed to separate as much honey as possible. The adhering honey and other impurities are next removed by melting the mass in boiling water, when the wax melts and floats on the surface. It is poured off into flat moistened vessels to cool, and is removed in cakes.

Pure wax is white, but from contact with the honey and pollen it acquires a colour, and the cakes are yellow, varying in tint according to the materials employed by the bees.

Wax has a pleasant honey-like smell, which is made more apparent by warmth, and it has a slight taste when chewed. The specific gravity at 15° is from 0·960 to 0·963; wax from the tropics is somewhat heavier, but does not exceed 0·966. When cold it is brittle; at ordinary temperatures it is tenacious, and its fracture is dry and granular. It softens when held in the hand, and melts at 62–64° to a clear oily liquid, which solidifies at once below the melting-point, without sensible evolution of heat.

It is insoluble in water and in cold alcohol, but more or less soluble in boiling alcohol, hot ether, benzene, carbon bisulphide, and chloroform. It is soluble in all proportions in the fats and oils.

Yellow wax has the composition C 79·3, H 13·2, O 7·5.

46–47 p.c. of it is saponifiable, and its proximate composition may be stated as 10 p.c. of cerin or ceryl cerotate $C_{27}H_{55}.C_{27}H_{53}O_2$, which is soluble in boiling alcohol; and 90 p.c. of myricin or myricyl palmitate $C_{30}H_{61}.C_{16}H_{31}O_2$ which is insoluble in boiling alcohol. But these percentages vary.

Besides these the wax contains substances possessing colour, taste, and smell, and a resinous yellow colouring matter, which remains dissolved when yellow wax is treated with hot spirit and the solution allowed to cool.

Wax boils at 236° and undergoes destructive distillation. It yields, however, no acrolein. The following are the products: first, a colourless watery distillate, 'wax spirit,' containing acetic and propionic acids; then a thick oil, mostly solidifying in the neck of the retort, 'wax butter' (*Butyrum ceræ*), consisting mainly of *cerotene* $C_{27}H_{54}$ and *melissine* $C_{30}H_{60}$ together with palmitic acid; and, lastly, a yellowish thin empyreumatic oil, 'wax oil,' which was formerly used medicinally both externally and internally, and consists mainly of hydrocarbons of C_nH_{2n} series.

Yellow wax is extensively employed in the arts and in pharmacy.

White wax. Yellow beeswax is not adapted to candle-making, as candles made from it burn badly and with a smoky flame. It is purified by repeatedly re-melting in hot water until it is no longer grey. In doing this the grey underlayer is cut off, and re-melted with the raw wax.

The next step is to destroy the yellow colouring matter, but chlorine and many other bleaching agents attack the wax and make it more brittle and friable, and thus cause it to lose its softness, and tallow has to be added to restore it. Chlorine further forms chloro-substitution products with the wax, and hydrogen chloride is liberated when the candle is burnt.

The best method of bleaching is to reduce the wax to thin strips or shavings so as to increase the surface as much as possible, and to expose it to moisture and sunlight. The melted wax is poured from a ladle into a square box of metal plate, in the bottom of which are several narrow slits. These slits are directly over a horizontal wooden roller revolving in a vessel filled with water which covers half the roller. The wax escapes from the slits in bands, which pass over the revolving roller and solidify in the water in the form of thin ribbons.

Another plan is to melt the wax in a rotating vessel of tinned copper provided with taps; from these the wax falls in drops or streams into ice-cold water. The grains or threads expose more surface, and the bleaching takes at least one-third less time, than when ribbons are used.

These ribbons, threads, or grains are removed from the water and spread on linen stretched over square wooden frames, and then exposed to the sun. Every day they are once or oftener sprinkled with water to keep them moist, and they are frequently turned over to expose fresh layers to the sun. After a longer or shorter period, depending on the intensity of the sunshine and the temperature, the bleaching is complete.

The wax is then once more melted in hot water, strained, and allowed to solidify in suitable shapes. The inner portion of the ribbon bleaches much less slowly than the outer surface, and the bleaching occupies twenty to thirty-five days or more. To accelerate the bleaching the partially bleached wax is re-melted and again made into ribbons so that new surfaces are exposed; this causes loss of from 2 to 10 p.c. Thread and granular wax rarely require re-melting. Wax from different sources bleaches with varying facility, and some cannot be bleached, so it is well first to try a sample on a small scale.

Since the sun-bleaching is properly due to the formation and action of either ozone or hydrogen peroxide, the action can be aided by melting together from 1 to $1\frac{1}{2}$ parts of rectified oil of turpentine, free from resin, with 8 parts of yellow wax, and then making into ribbons, and proceeding as above; this reduces the time to from six to eight days, at the end of which the smell of turpentine will have disappeared.

Wax bleachers frequently make additions to the wax—such as argol, alum, white arsenic—which, however, seem to have no great value. They are removed on re-melting the wax with water; or else additions of tallow, vegetable waxes, stearic acid, &c., are made to increase the whiteness of the wax after bleaching.

Wax in threads and grains can be very easily and well bleached by immersion in hydrogen peroxide, and also by treatment with dilute chromic acid or a mixture of potassium bichromate and sulphuric acid.

White wax is of a pure white colour, without taste or smell, and is comparatively hard and brittle, with a splintery fracture, translucent at the edges, softens at 30°, and at the temperature of the hand on kneading does not feel greasy, melts at 63–64°, behaves like yellow wax on solidifying, and has at 15° a sp.gr. of 0·965 to 0·969. Its solubility in the various media, its proximate and ultimate composition, are nearly the same as those of yellow wax.

Wax, both white and yellow, is very frequently adulterated; the specific gravity and melting-point are especially important in determining the quality. The most common adulterants are the following: (1) Water added to increase the weight; this can be recognised by the dull coarse fracture of the mass, and by gently heating and allowing to cool, when the water separates, and the quantity can be determined by weighing the cooled wax. (2) Powdery substances, such as ochre, brickdust, pea flour, heavy spar, clay, litharge, &c.; these substances separate when the wax is melted, and can thus be recognised. (3) Stearin, resin, and varieties of plant wax, which raise the specific gravity; and paraffin, ceresin, ozokerit, which lower it. Mixtures of alcohol and water of known specific gravity and at 15° can be used for examining the wax by observing whether it sinks, or hovers, or floats; the mixture should possess a sp.gr. of 0·965–0·970 for testing white wax, and of 0·955–0·965 for yellow wax. Paraffin can be recognised by warming the suspected wax with fuming sulphuric acid in a porcelain dish; pure wax is thereby completely destroyed, and changed into a black gelatinous mass, from which, on cooling, paraffin separates unaltered. (4) Tallow is tested for by cutting the wax into shavings, transferring these to a flask, pouring ammonia solution over them and warming: pure wax gives no cloud, but one is produced if tallow is present. Tallow may also be detected by soaking a wick in the wax, then lighting and extinguishing it, when a smell of acrolein will be observed if tallow is present. (5) Stearic acid; this can be detected by dissolving a small quantity of wax in ten times as much chloroform and adding lime water; pure wax remains dissolved, but if stearic acid is present a granular precipitate of calcium stearate is formed. (6) Resin is detected by boiling with concentrated nitric acid; if resin is present the liquid becomes reddish, and, on adding water, allowing to cool, and removing the wax, the liquid becomes cloudy and the resin separates as a yellow flocculent precipitate, which dissolves in caustic ammonia with a red-brown colour (*cf.* Schmidt, Seifens. Zeit. 49, 589; S. C. I. 2, 182). (7) Japan wax; this is detected by boiling about equal parts of borax and wax (1 grm.) with 15–20 times as much water; the milky or cloudy mixture separates slowly when at rest into a clear liquid, with solidified wax floating above. In the case of yellow wax the liquid is yellow; but if Japan wax is present the whole remains milky, and, according to the amount of adulteration, thick, or gelatinous and stiff (*v.* Oils, fixed, and fats).

Hübl's test (Chem. Zeit. 13, 1375) is the most trustworthy for the quantitative and qualitative examination of wax, and Röttger, having carefully examined the various other methods, has come to the conclusion that the result in most cases is very unsatisfactory. Two methods only are mentioned which give good results, if the adulteration of wax with stearic acid has to be proved:—

1. Fehling's method (D. P. J. 147, 227): The substance is boiled for four or five minutes with twenty times its weight of alcohol, and afterwards allowed to stand for several hours. Then it is filtered, and the filtrate mixed with water. If the wax was pure the liquid remains transparent; but if it was adulterated with stearic acid it loses its transparency, a reaction which is plainly perceptible even if the adulteration amounts to as little as 1 p.c.

2. Benedikt (An. der Fette, 291) advises boiling the substance with sodium carbonate. The solution, on cooling, becomes solid when sodium stearate is present. This method is also trustworthy, but is not so exact as that of Fehling.

The two methods just mentioned, together with Hübl's and the sp.gr. test, seem to be all we have practically to rely upon to prove adulteration in wax (H. Röttger, Chem. Zeit. 14, 606–607; S. C. I. 9, 771).

The test given in the U.S. Pharmacopœia is as follows: If 1 grm. of wax be boiled for half an hour with 40 c.c. solution of soda (sp.gr. 1·18), the volume being maintained by the occasional addition of water, the wax should separate on cooling without rendering the liquid opaque, and no precipitate should be produced in the filtered liquid by hydrochloric acid (absence of fats, or fatty acids, Japan wax, resin); nor should the same reagent produce a precipitate in water which has been boiled with a portion of the wax (absence of soap). If 5 grms. of wax be heated in a flask, for fifteen minutes, with 25 c.c. SO_4H_2 to 160°, and the mixture diluted with water, no solid wax-like body should separate (absence of paraffin).

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Carnaüba or Carnahuba wax is derived from the carnaüba palm (*Corypha cerifera*, Linn., or *Copernicia cerifera*, Mart.), which grows in Brazil, especially in the provinces of Ceara, Rio Grande do Norte, Piauhy, &c. The young leaves, of about three feet length, have a coating of wax on both the upper and under sides, which appears homogeneous to the naked eye. The wax layer is thicker on the upper side, and comes off in scales; on the lower side it is thinner and more adherent.

The leaves are carefully cut off from the tree and dried, and by beating and shaking the wax comes off in scales, or as a greyish white powder. This is either melted over an open fire or boiled with water, when the foreign matters fall to the bottom, and the wax floats and is removed.

Raw carnaüba wax is of a dirty greyish, yellowish, or greenish colour, very hard, brittle, and easy to powder. In its outward appearance it is compact, but penetrated with very many air spaces; it is tasteless, and smells when fresh somewhat like fresh hay—*i.e.* of coumarin; later, it becomes inodorous. It is purified by re-melting, and has then a greenish-yellow colour, which cannot readily be removed.

Freshly-purified wax melts at 85–86°, and solidifies at 80–81°. In the case of old wax the melting-point is 90–91°, the solidifying point is 86–87°, and the mass, after cooling, is somewhat crystalline. The wax, especially when fresh, on melting diffuses a slight odour, which is not unpleasant; on distillation it gives a paraffin-like product. The sp.gr. of the wax at 15° is 0·995 to 0·999.

In cold alcohol it is only partly soluble (melissyl alcohol), in boiling alcohol and ether it is completely soluble; the concentrated solutions solidify on cooling, with separation of a white crystallisable mass melting at 105°.

Carnaüba wax, on boiling with caustic potash solution, is coloured reddish; it is saponified with difficulty by alcoholic potash, and then only partially.

According to Stürcke (A. 223, 314), it contains:—

(1) A hydrocarbon, m.p. 59–59·5°.

(2) An alcohol $C_{26}H_{53}CH_2OH$, m.p. 76°.

(3) Myricyl alcohol $C_{29}H_{59}.CH_2OH$, m.p. 85·5°.

(4) A divalent alcohol $C_{23}H_{46}(CH_2OH)_2$, m.p. 103·5–103·8°.

(5) An acid $C_{23}H_{47}COOH$, m.p. 72·5°, isomeric with *lignoceric acid.*

(6) An acid $C_{26}H_{53}COOH$, m.p. 79°, identical or isomeric with cerotic acid.

(7) An acid $C_{19}H_{38}{<}\begin{matrix}CH_2OH\\COOH\end{matrix}$, an oxyacid corresponding to the lactone $C_{19}H_{38}{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$; m.p. 103·5°.

Compare also Bérard, Bl. [1] 9, 41; Story Maskelyne, C. J. 7, 87; Pieverling, A. 183, 344.

Carnaüba wax is extensively used in making candles and wax varnish, as much as 1,500,000 kilos. being yearly exported from the ports of N. Brazil, in addition to 850,000 kilos. retained for internal consumption.

Cow tree or Milk tree wax comes from the American cow tree or milk tree, *Palo de Vaca*, *Brosimum Galactodendron*), which grows on the mountains of S. America, and is especially abundant in the district from Barbula to Lake Maracaibo, and also at Caracas. This tree reaches a height of 30 metres, and has leathery leaves 30 to 40 centimetres in length, and resembling bay leaves in shape. When an incision is made in the trunk or branches a milky sap flows out, resembling cow's milk in colour and taste, but being of a thicker consistency and having a disagreeable smell. Unlike cow's milk, it is not coagulated by acids; in fact, it is somewhat acid itself, and, unlike other milky saps, it does not taste sharp or bitter. The milk flows so freely that in half an hour a litre bottle can be filled; the liquid is drunk by the natives like cow's milk, and it is also used for tea, coffee, or cocoa.

When exposed to the air, the milk forms a cheeselike skin. If the milk be boiled, the wax separates, to the extent of 30–35 p.c., as a yellowish resinous, waxy solid.

The wax is somewhat translucent, and can be kneaded; it melts at 50–52°, it is partially saponifiable, and in its external appearance it most resembles beeswax of all the vegetable waxes. It makes very good candles, burning with a bright flame. It is completely soluble in boiling alcohol (*v.* Marchand, J. pr. 21, 43).

Fig or Java or Getah wax comes from the wax fig tree, *Ficus ceriflua* or *F. cerifera*, Blume, which grows in Java, especially in the western and central districts; also in Sumatra and Ceylon. This tree contains a milky sap, which yields the wax on evaporation over an open fire and subsequent treatment with water. The wax has a reddish-brown colour, which in the interior becomes almost a rosy red. After bleaching it becomes a pure white; it is easily friable, softens at 45°, and melts at 56–57°. It is used in making candles.

Insect wax (also called *Chinese wax*, *vegetable spermaceti*, *tree wax*, and sometimes, but incorrectly, *Japanese wax*) is the secretion of an insect, *Coccus ceriferus*, Fabr., or *Coccus pela*, Westwood. The Chienchang valley, which is about 5,000 feet above the level of the sea, is the great breeding-ground of the wax insect. One very prominent tree there is known to the Chinese as the insect tree. It is an evergreen, with the leaves springing in pairs from the branches, very thick, dark-green, glossy, ovate, and pointed. In May and June the tree bears clusters of white flowers, which are succeeded by a fruit of a dark-purple colour. The Kew authorities have come to the conclusion that it is *Ligustrum lucidum*, or large-leaved privet. In March, when Mr. Hosie saw the trees, he found attached to the bark of the boughs and twigs numerous brown pea-shaped excrescences. The larger of these were readily detachable, and, when opened, presented either a whity-brown pulpy mass or a crowd of minute animals like flour, whose movements were just perceptible to the naked eye. From two to three months later these had developed in each case into a swarm of brown creatures, each provided with six legs and a pair of antennæ; each of these was a wax insect. Many of the excrescences also contained either a small white bag or cocoon covering a pupa, or a perfect imago in the shape of a small black beetle. This beetle is a species of *Brachytarsus*. If left undisturbed, the beetle, which is called by the Chinese the 'buffalo,' will, heedless of the *cocci*, continue to burrow in the inner lining of the scale, which seems to be its food—the beetle is, in fact, parasitic on the *coccus*. When a scale is plucked from the tree the *cocci* escape by the orifice which is made. Two hundred miles to the north-east of the Chienchang Valley, and separated from it by a series of mountain ranges, is the town of Chiating, in which insect wax, as an article of commerce, is produced. The scales are gathered in the Chienchang valley, and are made up into paper packets, each weighing about 16 ounces. Sixty of these packets make a load, and are conveyed by porters from Chienchang to Chiating (in former years there are said to have been as many as ten thousand of these porters). They travel only during the night, in order to avoid the high temperature of the day, which would tend to the rapid development of the insects and their escape from the scales. At the stopping-places the packets are opened out in cool places; but in spite of this, each packet is found to have lost on an average an ounce in transit. A pound of scales laid down in Chiating, in years of plenty, costs about half-a-crown; in bad years the price is doubled. In favourable years a pound of scales will produce four to five pounds of wax. In the plain around Chiating the plots of ground are thickly edged with stumps varying from 3 or 4 to 12 feet high, with numerous sprouts rising from their gnarled heads, and resembling at a distance our own pollard willows. The leaves spring in pairs from the branches, and are light-green, ovate, pointed, serrated, and deciduous. The tree is said to be in all probability the *Fraxinus chinensis*, a species of ash. On the arrival of the scales from Chienchang about the beginning of May, they are made up in small packets of from twenty to thirty scales, which are inclosed in a leaf of the wood-oil tree. The edges of the leaf are tied together with a rice straw, by which the packet is suspended close under the branches of this ash, or white-wax tree, as the Chinese call it. A few rough holes are drilled in the leaf with a blunt needle, so that the insects may find their way through them to the branches. On emerging from the scales the insects creep rapidly up the leaves, among which they nestle for a period of thirteen days. They then descend to the branches and twigs, on which they take up their position, the females doubtless to provide for a continuation of the race by developing scales in which to deposit their eggs, and the males to excrete the substance known as white-wax. This first appears as an undercoating on the sides of the boughs and twigs, and resembles sulphate of quinine, or a covering of snow. It gradually spreads over the whole branch, and attains, after three months, a thickness of about a quarter of an inch. After the lapse of a hundred days the deposit is complete, the branches are lopped off, and as much of the wax as possible is removed by hand. This is placed in an iron pot of boiling water, and the wax, on rising to the surface, is skimmed off and placed in a round mould, whence it emerges as the insect wax of commerce. Where it is found impossible to remove the wax by hand, the twigs and branches are thrown into the pot, so that this wax is darker and inferior. The insects, which have sunk to the bottom of the pot, are placed in a bag and squeezed of the last drop of the wax, and are then thrown to the pigs (*Nature*, January 29, 1891).

Insect wax is quite different from Japan wax, though often confounded with it. It is of a white colour, with a trace of yellow, and has a crystalline structure. It is very like spermaceti in appearance, but more fibrous and considerably harder, and can almost be powdered. It has no taste or smell; its sp.gr. at 15° is 0·970; it melts at 82° to 83°; it is very slightly soluble in alcohol and ether, but is very easily soluble in benzene, from which it can be obtained in a crystallised state. It is only saponified by boiling potash with great difficulty. It is composed of *ceryl cerotate* $C_{27}H_{55}.C_{27}H_{53}O_2$ in a nearly pure state.

In China and Japan it is used for making candles, which give a much better light than ordinary candles. Candles made from the fat of *Stillingia sebifera* (Micha.) receive an outer coating of this wax to prevent guttering. Other uses are for polishing furniture and leather, as a sizing for paper and cotton goods, for imparting a gloss to silk, and also externally and internally in medicine.

Japan wax is the most largely utilised of all the plant waxes. It is obtained from *Rhus succedanea* (L.), and from one or two other species of *Rhus* growing in China and Japan; but the export from China is very small in proportion to that from Japan. In *R. succedanea* the wax lies among the fibres of the pericarp of the fruit, which is about the size of a pea. To obtain the wax, the fruit, either whole or freed from its kernel, is either bruised or else ground between the millstones. The mealy product is boiled with water in large kettles, the wax is skimmed off, and after several re-meltings to remove impurities is cast into tablets. Another plan is to first thrash the fruit, then, after drying for fourteen days, to slightly roast it and grind it between millstones. The meal is then placed in linen sacks, subjected to the action of steam, and pressed in a screw press.

Recently ether or carbon bisulphide have been employed to extract the wax, and the resulting wax is not so green as that obtained by pressing, so the pressed wax is bleached to improve its colour by breaking small, planing, washing with water, and exposing to the sun, and the products are classified, according to the degree of bleaching, as raw wax, second wax, and first wax.

In order the better to get out the wax left in the residue, an addition of 10 p.c. of perilla oil (the oil from *Perilla ocymoides*, L.) is repeatedly added. This affects the consistency of the wax, and is the reason why both soft and hard varieties of the wax are met with in commerce.

The wax comes into the European trade in the form of flat, round discs or cakes, 2 to 3 centimetres thick and 10 to 12 centimetres across. They are of a pale-yellow colour, and have a greasy feel. The cakes are sometimes in the form of square tables of the same dimensions, and these are more easily packed. These cakes are made by pouring the melted wax into clay dishes. They have a waxy appearance, but are whiter than beeswax, and have an even or a conchoidal fracture. The freshly-broken surface is dull, but a cut surface has a waxy lustre. The wax can be kneaded between the fingers, and has a somewhat resinous, tallowy, and rancid smell and taste. On long keeping it becomes yellow or brownish, and if it contains much water becomes covered with a white dusty growth.

Under the microscope the interior of the wax proves to be composed of smaller and larger granules, with different refracting powers, and between these grains there occur needle-shaped crystals of palmitic acid. The yellow outer portions have the same nature, only they contain more crystals than the interior, and the white covering is rich in stick-like and broad prismatic crystals.

Japan wax melts at 53·5–54·5°, solidifies at 40·5–41°, and in solidifying the temperature rises to 45·5–46°. The wax has the property of becoming transparent when warmed to a temperature 10 to 12 degrees below its melting-point. This is one of the reasons that its melting-point has been differently stated by various authorities, who give numbers varying from 42° to 55°. If the wax is melted afresh a short time after solidifying it melts at 42°, and only after a long time recovers its usual melting-point of 53·5°. The sp.gr. of the bleached wax at 15° is from 0·970 to 0·980.

Japan wax is insoluble in cold alcohol, but is easily soluble in boiling 97 p.c. alcohol, and the solution on cooling solidifies to a white granular, crystalline mass. Ether dissolves very little in the cold, and a hot ethereal solution deposits flocks on cooling. The wax is readily soluble in benzene and in petroleum spirit.

It mainly consists of glyceryl palmitate $C_3H_5(C_{16}H_{31}O_2)_3$. It contains glyceryl, also arachidate and stearate, amounting to 6·2 p.c., and also some free palmitic acid. Its ultimate composition is

		Wax purified by ether
C . . .	70·00	73·12
H . . .	12·07	11·85
O . . .	17·93	15·03
	100·00	100·00

It is characterised by the ease with which it can be saponified, and also by the small amount of ash it contains (0·02 to 0·08 p.c.). It is liable to adulteration with water and tallow up to 30 p.c.

In the East Indies Japan wax is used instead of tallow for making candles, and also for giving a polish to turned woodwork. In Europe it is used for the same purposes, and also for making wax matches, and for adding to bleached beeswax in the manufacture of wax candles in order to help the loosening of the candle from the mould after it is cast. It is also used to adulterate white beeswax. Owing to its more or less rancid nature it is scarcely used in pharmacy and perfumery, but it is employed in preparing castor-oil pomade, as the mixture by repeated meltings becomes transparent.

Myrtle berry wax is obtained from the wax myrtle, *Myrica cerifera* (Linn.), a shrub growing on peaty soil in North America. The fruit is brown or blackish, and of the size of a pea; it secretes the wax, and becomes covered with a snow-white crust penetrated by brown or black points of the fruitskin, so that the wax can only be got off as a powder, and not in coherent pieces. The wax is also got from other Myricaceæ—namely, *M. carolinensis* (Mill.) in North America; *M. caracassana* (Humb. and Bonpl.) in South America, especially in Columbia and Venezuela; *M. cordifolia* (Linn.); *M. quercifolia* (Linn.) and *M. serrata* (Linn.), in the Cape of Good Hope; and *M. æthiopica* (Linn.), in Abyssinia.

To obtain the wax, the berries are boiled with water, and the fatty mass that floats on the surface is skimmed off and poured into flat dishes; the yield of wax is from 20 to 25 p.c.

The wax which comes from the United States has a deep-green colour, due to chlorophyll; this colour is bleached to a greyish-yellow by exposure to light and air for several years; but the change extends only a few millimetres below the surface. The taste and smell are feeble and balsam like; the Hottentots eat the wax like cheese. It is harder than beeswax. The specific gravity of the wax at 15° is 1·000 to 1·005; the melting-point is 45°–46°. Cold alcohol and ether dissolve only very little of the wax, but it is soluble in 20 parts of hot alcohol, leaving palmitin undissolved. Four-fifths separate on cooling; 4 parts of boiling ether dissolve 1 part of wax, most of which is deposited in an uncoloured condition, when the ether cools, and the liquid remains a fine green. Cold oil of turpentine only softens the wax, fatty oils dissolve it more readily. It is easily saponified by alkalis. It contains much palmitic acid, with little myristic and stearic acids, mostly free, but a little as glycerides. There is no oleic acid present, and it contains ·17 to ·20 p.c. of ash.

It is used like beeswax, but, owing to its inferior ductility and plasticity, beeswax is mixed with it when worked. It is liked in America for making candles, owing to their giving a pleasant smell when extinguished.

Ocuba wax comes from the nutmeg tree *Myristica ocuba* (Humb. and Bonpl.), which grows as a shrub in Brazil and in Guiana. The fruit is of the size of a small hazel nut, and the seed is covered with a purple-red mantle. The fruit, which yields 18 to 20 p.c. of wax, is reduced to small pieces and boiled with water, when the wax separates as a layer on the surface, and is removed when cold. It is of a yellowish-white colour, and whiter than beeswax; its specific gravity at 15° is 0·920, and it melts at 39°–40°. It is very slightly soluble in cold alcohol, but is completely soluble in boiling alcohol and ether. It is used for making candles, but always in admixture with other materials, owing to its low melting-point.

Palm tree wax, also known as *Cerosiline* and *Ceroxylin*, comes from the common wax palm or Andes wax palm *Ceroxylon andicola* (Humb. and Kunth), and also from the Klopstock palm *Klopstockia cerifera*, Kausten. The first of these grows in the West Indies and on the Andes in South America at an elevation of 2,000 to 3,000 metres; the stem is 60 to 65 metres high, and the feathery leaves are 6 to 8 metres long. The second palm, which grows in Columbia, also has feathery leaves, and reaches the same height. Both secrete a resin-like wax, especially out of the rings of the stem, which cover the stem with a mass of crusts reaching 6 millimetres in thickness.

The wax is scraped off from the stem, and forms a greyish-white powder; a man can daily cut down and scrape two trunks, and thus get 25 kilos. of wax, which is melted over a fire, and is purified by re-melting. Another method is to boil the bark with water; the wax does not melt, but only softens, and the impurities deposit themselves. The wax thus obtained forms a yellow or yellowish-white mass, and comes into commerce either in lumps or in the form of balls. Its fracture is conchoidal, and in hardness it is like carnaüba wax. The raw and purified wax has a specific gravity at 15° of 0·992 to 0·995; it softens by the warmth of the hand, but only melts at 102–105°. It is a mixture of wax and a resin; on dissolving in much boiling spirit, and allowing to cool, the wax separates as a somewhat crystalline mass, and can be purified by repeated washing, and recrystallisation from boiling spirit. This pure wax is a whitish-yellow substance, similar to beeswax, and it melts at 72° to a liquid with a slight colour. Like carnaüba wax, it contains ceryl cerotate and melissyl palmitate.

Mixed with a small amount of tallow to diminish its brittleness, palm-tree wax is made into candles. It cannot be bleached, so the candles have a lemon-yellow tinge.

Spermaceti or **cetine** occurs in special cavities of the skull-bones and in the blubber and other parts of the sperm whale *Physeter macrocephalus* (Linn.), also in other cetaceæ, such as *Delphinus tursio* (Linn.), and *D. edentulus* (Linn.). Spermaceti is also found in small quantity in the blubber of *Balæoræa rostrata* and in the oil of *Delphinus globiceps*, *Hyperoodone rostratus*, and *H. bidens*. The spermaceti exists in the sperm whale, held in solution in the sperm oil at the temperature of the animal's body, but after death it separates out in a crystalline form. It is strained off and pressed, and treated with a weak solution of caustic potash or soda to saponify the adhering oil; it is then washed with water, and re-melted in boiling water. Raw spermaceti is in the form of yellowish and translucent plates, possessing a leafy structure and a rancid fishy smell, but it rarely occurs in commerce in this state. After the treatment with alkali, it is obtained in white translucent pieces with a broad leafy crystalline structure, and with a feel like talc or soapstone; it is nearly without taste and odour, and can be rubbed to powder. The specific gravity at 15° is 0·943, and the melting-point lies between 50° and 54°; the solidifying point is below the melting-point. If spermaceti be purified by repeated treatment with hot alcohol, the product has a melting-point some 5° higher, and can be distilled at 360° without perceptible decomposition.

Spermaceti is insoluble in water, very slightly soluble in cold alcohol, benzene, and petroleum ether. 40 parts of boiling alcohol of specific gravity 0·830 dissolve 1 part of spermaceti; on cooling, the greater part separates again in a crystalline condition. It is very readily soluble in ether, chloroform, and carbon bisulphide.

Spermaceti is a mixture of different esters, but does not contain glycerides; by recrystallisation from spirit of wine there separates *cetyl* or *hedecatyl palmitate* $C_{16}H_{33}.C_{16}H_{31}O_2$. The alcohol leaves on evaporation an oil, the *cetinelain* of Berzelius, which saponifies with difficulty, giving *cetinelaic acid*, which is distinguished from oleic acid in that it forms a lead salt insoluble in ether, and gives no acrolein on dry distillation. Spermaceti is saponified with great difficulty. Besides cetyl palmitate it contains small quantities of other compounds which give on decomposition stearic, myristic, and laurostearic acids, as well as the corresponding alcohols, which Heintz (P. 81, 267, 553) calls *steathal* $C_{18}H_{38}O$, *methal* $C_{14}H_{30}O$, and *lethal* $C_{12}H_{26}O$.

The ultimate composition of spermaceti is:

C	80·03 p.c.
H	13·25 ,,
O	6·72 ,,
	100·00 ,,

Spermaceti is not easily adulterated, since every admixture causes it to lose to a great extent its characteristic properties. Wax is to some extent mixed with it, but it should not be so abundant as to make the specific gravity materially higher or the solution in ether milky. Tallow can be detected by the smell when melted, or by the smell of acrolein, noticed when a wick soaked with the spermaceti is lit and blown out; also by the substance giving grease spots on paper. Stearic acid makes it harder, and causes it to crystallise in smaller leaves, and the doubtful spermaceti, when boiled with soda solution, produces a foam. The presence of paraffin can be tested for by means of fuming sulphuric acid, as in the case of wax.

Spermaceti becomes yellowish and rancid on long exposure to air, but can be purified by remelting and treating with dilute caustic soda. Spermaceti can be distinguished from stearin by its being scarcely attacked when boiled with dilute sodium carbonate.

It is used for making candles, which burn brightly and without smell; also for dressing fabrics. In pharmacy it is a frequent constituent of cerates, salves, and cosmetics. *V.* Chevreul, A. Ch. [1] 7, 157; Dumas and Péligot, A. Ch. [1] 62, 5; Heintz, P. 81, 267, 553.

H. H. R.

WAX VARNISH *v.* VARNISH.

WEISSENFELS LIGNITE RESINS *v.* RESINS.

WEISSGÜLTIGERZ *v.* FREIBERGITE.

WELD. This yellow dye-stuff is the dried herbaceous plant known as *Reseda Luteola.* It is a native of Europe, and has long been cultivated in many parts, especially in France and Germany. It is said to be the oldest European yellow dye-stuff known, having been employed by the Gauls and other ancient nations. At present it is little employed, and its cultivation in this country has long been discontinued. The plant attains a height of about a yard, it has a stiff, straight main stem and several similar upright flowering branches. It is sown in June, and gathered, when seeding, in the following year, being then pulled up by the roots, dried in the open air, and sold in sheaves. The colouring matter, which is disseminated throughout the entire plant, resides chiefly in the leaves, seeds, and upper portions of the stems.

Luteolin, the colouring matter of weld, was first isolated in the pure condition by Chevreul. Moldenhauer's method of obtaining it consists in extracting the dried plant with hot alcohol, 80 p.c. From the concentrated extract crude luteolin separates on long standing; after dissolving it in hot concentrated acetic acid, the solution is filtered and cooled, and the separated luteolin is washed with water and dried *in vacuo.* Resinous impurity is then removed by washing slightly with ether, and it is then dissolved successively in ether and alcohol; the latter solution is considerably diluted with water, then boiled and allowed to cool, when pure luteolin crystallises out.

Another method is to precipitate the alcoholic extract of weld with lead acetate, decompose the precipitate with hydrogen sulphide, extract the luteolin from the dried precipitate with aqueous ether, and crystallise from alcohol, or from dilute sulphuric acid, acetic acid, or water mixed with a little alcohol.

Schützenberger and Paraf employ a simple process for preparing pure luteolin, based on the fact that it dissolves in considerable quantity in superheated water, from which it crystallises on cooling, leaving resinous impurities undissolved. The greenish flocculent precipitate of impure luteolin, obtained on adding water to an alcoholic extract of weld, is suspended in water and put into an ordinary strong sealed tube, or into a glass tube closed at one end and placed in a strong steel or copper cylinder fitted with a screw cap. After heating to 250°C. for about twenty minutes and then allowing to cool, the upper portion of the clear liquid is found to contain numerous crystals of luteolin, while the resinous impurity remains at the bottom. The latter yields more luteolin by a further similar treatment, and the luteolin obtained may also be purified by repeating the process.

Pure luteolin crystallises in yellow quadrangular silky needles, frequently forming star-shaped groups. It has a bitter, astringent taste; it melts about 320°C., and sublimes, with partial decomposition. It is very sparingly soluble in cold water, more readily in hot water, slightly in ether, but very soluble in alcohol. In caustic and carbonated alkalis it dissolves freely with a deep-yellow colour, and in concentrated sulphuric acid with an orange-red colour; from the latter solution it is precipitated unchanged on addition of water. Although little soluble in dilute acids, it is very readily so in hot concentrated acetic acid. According to Chevreul, it unites with acids. Nitric acid converts it into oxalic acid. Heated to 200°C. with phosphoric anhydride, luteolin is converted into a red substance, soluble in ammonia with a violet colour. Melted with caustic potash, luteolin yields protocatechuic acid, and probably also phloroglucin. By the action of sodium amalgam on an acidulated alcoholic solution of luteolin, the solution acquires a purple colour similar to that given by morin and quercitrin under similar conditions. An aqueous solution of luteolin is coloured green by ferric chloride, with lead and aluminium it forms yellow precipitates. Luteolin does not appear to be a glucoside. Its true composition is still unknown, and various formulæ have been assigned to it. Schützenberger and Paraf give it as $C_{12}H_8O_5$ when dried at 150°C., or with one molecule of water when dried over sulphuric acid. Moldenhauer gives it the formula $C_{20}H_{14}O_8$, and Hlasiwetz $C_{15}H_{10}O_6$, considering it to be isomeric with paradiscetin.

The importance of weld as a dye-stuff in silk- and wool-dyeing has greatly diminished in consequence of its low colouring power compared with quercitron bark and flavin, and more recently by reason of the introduction of certain permanent yellow colouring matters derived from coal-tar. Still it has valuable special properties as a dye-stuff. In conjunction with aluminium and tin mordants, it yields very bright pure lemon-yellow colours, fairly fast to light and soap, and not changing to an olive or reddish tint, as is the case with other vegetable yellows. With chromium and iron mordants, weld gives yellowish and greenish olives respectively. For yellow, wool and silk are mordanted with alum and tartar in the ordinary manner, and dyed subsequently in a decoction of weld with the addition of chalk to the dye-bath. Weld-alumina yellow is a standard colour for certain army cloths in this country. For silk dyeing weld-extract is still much sold, chiefly for the production of yellow and olive colours. Formerly, weld was much employed for the manufacture of a yellow alumina-lake, for the use of artists and decorators.

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WELDING (*Soude*, Fr.; *Schweissen*, Ger.) is the joining of two pieces of metal under the hammer at a sufficiently high temperature.

WESELSKY'S DYES *v.* Oxazine colouring matters.

WHALE OIL *v.* Oils, fixed, and fats.

WHEEL ORE *v.* Bournonite.

WHETSLATES *v.* Whetstone.

WHETSTONE. Some of the finest whetstones for sharpening edged tools, such as the 'Arkansas stones,' are made from *novaculite*, a rock so called from *novacula*, a razor. The sharpening quality is said to be due to the presence of disseminated crystalline silica, or, in some varieties, to minute crystals of garnet or rutile. The rock is so hard that it has to be cut with diamond dust. Some of the pure white novaculite seems to be a siliceous deposit from hot springs, whilst other varieties are altered schistose rocks of fine grain. The so-called 'Hindostan whetstone' is worked in the State of Indiana, whilst the stone known as 'chocolate whetstone' is a mica schist from New Hampshire. The famous 'German razor hones' are formed of a fine-grained argillaceous rock, occurring in slate near Ratisbon. The Scotch 'snake stone' or 'Water-of-Ayr stone' is used for rubbing down the surfaces of other stones and of copper-plates. 'Tam o' Shanter hones' are employed as ordinary whetstones. Coarse whetstones, used chiefly for scythes, have been worked for many years near Blackdown in Devonshire, and are known as 'Devonshire batts.' They are made from siliceous concretions embedded in sand, probably of Upper Greensand age. Somewhat similar scythe stones have been worked at Penzlewood, near Stourton in Wiltshire (H. B. Woodward, Geol. Eng. 1887; Renard, Mem. Ac. R. Belgique; Rep. Geol. Surv. Arkansas, 1890, vol. 3, 'Whetstones,' by L. S. Griswold); *v.* Oilstone.

WHISKEY *v.* Alcohol.

WHITE ANTIMONY. *Valentinite* *v.* Antimony.

WHITE ARSENIC. *Arsenious oxide* *v.* Arsenic.

WHITE COPPERAS. Native *ferric sulphate* or *cinquinolite* $Fe_2(SO_4)_3.9H_2O$.

WHITE FLUX *v.* Flux.

WHITE IRON PYRITES. *Ferric sulphide* or *marcasite* FeS_2, *v.* Iron.

WHITE LEAD *v.* Lead; also Paints and Pigments.

WHITE METAL *v.* Tin.

WHITE MUNDIC. *Mispickel* *v.* Arsenic.

WHITE PRECIPITATE. *Mercuric ammonium chloride* *v.* Mercury.

WHITE TELLURIUM *v.* Tellurium.

WHITE VITRIOL. *Zinc sulphate.* $ZnSO_4 7H_2O$ *v.* Zinc.

WHITING. Washed and levigated chalk.

WILLESDEN FABRICS AND PAPER *v.* Cellulose.

WILLIS'S LUTE *v.* Lutes.

WINE. Wine, strictly speaking, is the fermented juice of the *Vitis vinifera*. The term *British wines* is applied to beverages made after the manner of wine from substances other than the juice of fresh grapes.

The vine is cultivated for the manufacture of wine in the middle and south of Europe, the northern and southern extremities of Africa, some of the western parts of Asia, the islands of the Atlantic, portions of America—from the Potomac in the north to the centre of Mexico in the south—in California, and in Australia. The number of varieties is very large; but experience shows that the vines employed in particular districts should either be indigenous to those districts or be improved varieties of the indigenous strain. Thus, European vines when tried in America were but partially successful; whilst, on the other hand, American vines transplanted to the Gironde degenerated and yielded no potable wine. The vine grows on chalky, siliceous, aluminous, and magnesian soil, best along the borders of rivers, and on ground which, though not itself soaked with water, can constantly attract it from the subsoil (*v.* Thudichum and Dupré's Treatise on the Origin, Nature, and Varieties of Wine, 46–99; Lenoir's Traité de la Culture de la Vigne; Guyot's Viticulture).

Vintage and vinification. The methods of procedure vary with the character of the wine —*i.e.* whether white or red wine is to be produced. The practice as regards the period of ripeness at which the grape is gathered varies considerably; thus, in the case of champagne, where the greatest attainable paleness is desired, the grapes are gathered before the point of fullest maturity, whereas the wines of Burgundy are vintaged when the grapes produce the deepest colour. Wines from imperfectly-ripened grapes require longer time to mature after manufacture, and, theoretically speaking, the grapes should hang until excessive dryness or danger of frosts threaten; but other and conventional considerations, such as colour, have to be taken into account. In exceptional instances, as in the Sauterne district, those berries only are cut out of the bunch which have attained the desired point of ripeness; but the common practice is to gather all the grapes carried by the vines, the vintagers either separating immature and spoiled berries as they proceed, or carrying the whole bulk to a kind of specialist, who performs this part of the labour. Whichever course may be taken, the selected fruit is carried to the press house, and the question then arises whether the stalks are to be removed or pressed with the grapes. In the case of white wines the almost universal practice is to leave the grapes upon the stalks, for the reason that the resulting liquor is almost at once separated from the marc, and before the astringent principle of the stalks can be communicated to it, whereas in the case of red wines they must be allowed to remain upon the marc for some time, and the stalks are removed. The commonest mode of separation is to cause the grapes to pass through a series of sieves, by which the stalks are retained. The grapes are now crushed, either by being trodden underfoot in vats or by being passed through machines furnished with grooved rollers, the one thing to be avoided in either case being the bruising of the seeds and stalks if these have not been removed. The next process is pressing. The machines employed for this purpose were formerly boxes, so made that the must was expelled through apertures by superincumbent pressure exerted by a screw; but latterly centrifugal machines have been employed, with a saving of labour and time. In white wines the must is separated as much as possible from the marc before pressing; whilst in the preparation of champagne the grapes are not crushed at all previous to being placed in the press. In the case of red wines the colour is obtained by allowing the juice from the crushing to ferment, after which it is stirred with the grape husks, whereby the requisite amount of colouring matter is dissolved. So much of the must as can be drawn off by taps is run off by that means, and the marc is pressed; the two portions of the must are then added together. The proportion of must depends upon whether the stalks are removed or not; in the former case it is about 95 to 97 p.c. of the whole, in the latter it may only be 70 p.c.

Fermentation. White wines are generally fermented at a temperature of 10° or 12° in barrels with only the bunghole open for the escape of carbonic acid gas. Red wines are ordinarily fermented in vats open at the top, on account of the bulk caused by the retention of the husks and the necessity of stirring, an operation variously performed during or at the completed period of fermentation, according to the district. When fermentation is completed —*i.e.* after 10 to 14 days—the liquor has become clear, the yeast cells and other suspended matters are deposited at the bottom of the vessel, and the 'young' wine is racked off and allowed to rest for some time, after which it is again racked into clean casks in order to mature.

The young wine slowly loses its sugar by after-fermentation, and albuminous substances, colouring matters, together with the acid potassium tartrate, and calcium tartrate, separate out, forming a crust known as *argol* or *argal* (*q. v.*; also Tartaric acid).

The general nature of grape-juice may be seen from the following analyses by Neubauer of musts obtained in the Rhine district in 1874 (Fr. 15, 201, 1876):—

	Steinberger		Marcobrunner	
	Selected	Second quality	Selected	Second quality
Sugar	18·59	16·35	18·94	16·62
Free acid	0·53	0·60	0·60	0·60
Albuminoids	0·25	0·26	0·27	0·23
Mineral matter	0·29	0·27	0·28	0·28
Extractive matter	4·71	4·21	4·13	4·05
	24·37	21·69	24·22	21·78
Water	75·63	78·31	75·78	78·22
	100·00	100·00	100·00	100·00
Sp. gr.	1·0949	1·085	1·0969	1·087

Systematic examinations of the musts produced in various parts of Germany are now annually made and published in Fresenius' Zeitschrift für analytische Chemie. (For a series of determinations of the sp.gr. acidity, and ash of grape juice from different wine-producing districts *v.* J. Carter Bell, An. 4, 197.)

The higher the temperature the sooner the fermentation is finished; at low temperatures a moderate fermentation takes place, which becomes more violent as the liquid becomes warmer, and reaches a maximum at 27°. By the employment of high temperatures a must rich in sugar can be converted into a wine feebly alcoholic, sweet, and yet having tasting properties. Medium musts are best fermented at from 20° to 24°, and this temperature is reached when the fermentation begins at 15° (Müller, B. C. 1883, 783; C. J. Abst. 1884, 647). A temperature of 100° is not fatal to the fermentation of must, provided the latter contains oxygen.

Influence of the 'marc' on wine. By allowing the skins and stones of ripe grapes to remain in contact with the must, the resulting wine is said to improve in bouquet &c., and is less liable to become stale and ropy. In order to redden wine with the skins of black grapes the temperature of the wine should be between 15° and 17°. Bad grapes impart to white and red wines a brown colour. Such wines soon become turbid. Bad grapes and mildewed skins, as well as bad casks and puncheons, precipitate the red colouring matter, so that the wine becomes pale. The following are some of the cases in which the treatment of wine with 'marc' has been successful:—Wine which is muddy and cannot be clarified by the ordinary fining agents; wine in which a fining agent has been used which failed to sink to the bottom; wine which has become weak and flat; wine which is assuming or has assumed a black colour; wine having a barrel taste or a by-taste; wine which is 'corked'; wine remaining after casking off; and wine which is obtained by pressing the lees. In cases where the fermentation of new wine has been checked suddenly, the addition of marc prevents the separation of yeast (J. Nessler, C. C. 1882, 265; C. J. Abst. 1882, 1014).

The second fermentation of light wines rich in sugar, such as the '*vins de coupage*' when kept in casks for daily consumption, may be prevented by carefully heating the wine to 55–60° in a specially-constructed apparatus, and storing it in casks previously well washed with boiling water. The air which enters the flask when the wine is drawn off is filtered through cotton wool. This treatment does not appreciably affect the composition, colour, flavour, or any other property of the wine (Houdart, C. R. 97, 55). When wine becomes sour there is a diminution in the amount of extract matter, and gum, sugar, and other substances which decompose Fehling's solution disappear completely. Glycerin also decreases in quantity, as also does the cream of tartar, whilst the free tartaric acid disappears altogether. On the other hand, the potash increases in quantity, owing to the decomposition of the deposit of cream of tartar (Carles, B. C. 1883, 790).

Wine contains alcohols, glycerin, acids, salts, extractive matter, and those principles which give to it its particular colour, special flavour, smell, or bloom (*bouquet, Blume*). Whilst some of the constituents can be accurately isolated and described, others can only be detected by the smell. The principal alcohol is ethyl alcohol. In rare instances some butyl alcohol, and in others amyl alcohol, together with ethylene glycol and isobutyl glycol (Henniger), are present. The quantity of alcohol in natural wines from grapes varies from 6 to 12 p.c., and the quantity of glycerin from 7 to 10 p.c., of the alcohol present. The acids present are tartaric, malic, and tannic acids, due to the original grape juice. These greatly aid in the preservation of the wine by preventing the formation of fungi. As regards the origin of the fixed vegetable acids of wine, H. Brunner points out (C. C. 1877, 4) that malic, succinic, glycollic, and oxalic acids—which are found in unripe grapes, together with tartaric acid—may either be formed by direct building up of the molecules in the plant, or their formation may be partly direct and partly indirect. The latter assumption seems to agree best with laboratory results, and the following series, starting from the hypothetical carbonic acid CO_3H_2, may represent the gradual change of carbonic acid into other vegetable acids under the reducing influence of light:—

$$\underset{\text{Carbonic acid}}{2CH_2O_3} + H_2 = \underset{\text{Oxalic acid}}{C_2H_2O_4} + 2H_2O\,;$$
$$C_2H_2O_4 + H_2 = \underset{\text{Glyoxylic acid}}{C_2H_2O_3} + H_2O\,;$$
$$2C_2H_2O_3 + H_2 = \underset{\text{Tartaric acid}}{C_4H_6O_6}\,;$$
$$C_4H_6O_6 + H_2 = \underset{\text{Malic acid}}{C_4H_6O_5} + H_2O\,;$$
$$C_2H_2O_3 + H_2 = \underset{\text{Glycollic acid}}{C_2H_4O_3}\,;$$
$$C_4H_6O_5 + H_2 = \underset{\text{Succinic acid}}{C_4H_6O_4} + H_2O.$$

This series of transformations is supported by various chemical observations. It is known that formic and oxalic acids are the first reduction-products of carbonic acid. When other reducing agents—*e.g.* hydrogen—act on oxalic acid in the form of ethyl oxalate, glyoxylic acid is first formed, and from this acid either glycollic, tartaric, or deoxalic acid is obtained, according to the number of molecules added to the molecule of hydrogen, thus:—

$$\underset{\text{Glyoxylic acid}}{C_2H_2O_3} + H_2 = \underset{\text{Glycollic acid}}{C_2H_4O_3}\,;$$
$$2C_2H_2O_3 + H_2 = \underset{\text{Tartaric acid}}{C_4H_6O_6}\,;$$
$$3C_2H_2O_3 + H_2 = \underset{\text{Deoxalic acid}}{C_6H_8O_9}.$$

The change of oxalic acid and glyoxylic acid by hydrogen is well known; the formation of tartaric acid from glyoxylic acid by the same reaction was demonstrated by Debus in 1873, and it is further known that tartaric acid is easily transformed by reducing agents into malic acid, and thence into succinic acid. Brunner therefore believes that the same successive reactions go on in the plant; that malic and succinic acids contained in the grapes are derivatives of previously-formed tartaric acid, and that the latter is produced by the influence of light in the chlorophyll cells from carbonic acid and water, glycollic glyoxylic, and oxalic acids occurring as intermediate bodies. The juice of unripe grapes appears, in fact, to contain malic, glycollic, and succinic acids, in addition to tartaric; and in the juice of very young grapes, gathered just after the flowers had withered, Brunner and Brandenberg have found an acid exhibiting the characters of glyoxylic acid. The occurrence of succinic acid in grape juice is in accordance with the fact that this acid is also found in wine. It is, indeed, erroneous to impute the total acidity of wine to tartaric acid, inasmuch as succinic acid is often present in much larger proportion (C. J. Abst. 1877, 883). Carbonic, acetic, formic, and succinic acids, in addition, are products of fungi fermentation. Traces of other fatty acids—such as propionic, butyric, and œnanthic acids—are also present in wine, together with acetaldehyde, and possibly its homologues. Tartaric acid occurs mainly as the dextro- variety; lævo- tartaric acid is only of comparatively infrequent occurrence. If tartaric acid is not found—as, for example, in certain samples of sherry—its absence is probably due to its removal by 'plastering,' to which reference is made later on. The amount of free acid in sound wine, reckoned as tartaric acid, varies between 0·3 and 0·7 p.c.; a greater amount than this imparts sourness to the wine. The characteristic smell of wine is said to be due to œnanthic ether. These compound ethers probably confer the bouquets which distinguish one vintage from another. Among them are aceto-propylic, butylic, amylic, caprylic, butyro-ethylic, caprylo-ethylic, capro-ethylic and pelargo-ethylic, and the tartaric ethers.

According to Jacquemin (C. R. 110, 1140), the characteristic bouquets of wines are due to the special characters of the yeast used in each district. One and the same must fermented with the yeast obtained from several different districts gave wines having the bouquet characteristic of the district from which the particular yeast had come.

Babo states that the bouquet of the wine from Riesling grapes is produced by the action of frost; wines from other grapes also possess a like bouquet if the grapes are frozen. Rommer (Bl. [3] 2, 297) fermented the juice of an inferior grape and of hot-house grapes respectively with yeast cultures obtained from the Champagne, Côte d'Or, and Baxy districts, and found that in each case the wines had the bouquet of those from which the yeast has been derived.

According to Berthelot, the amount of the ethers in wine is, after a certain time, a constant quantity independent of the nature of the alcohols and acids, but a function only of their relative amount: If A be the percentage weight of alcohol in the mixture, a the amount of alcohol equivalent to the total free acid contained in one litre of wine, on the assumption that it is acetic acid (46 alcohol = 60 acetic acid), y the proportion p.c. of a present as compound ether in one litre of wine when the alcoholic strength of the wine is A, and x be the amount of alcohol present in the compound ethers of one litre of wine; then

$$y = 1{\cdot}17A + 2{\cdot}8$$

$$x = \frac{y \times a}{100}$$

The alcohols other than ethylic alcohol present are left out of the account, but as they are insignificant in amount the error is trifling. This formula affords a mode of judging of the age and genuineness of wines. The alcohol contained by the decomposition of all the ethers rarely exceeds 0·06 p.c. of the wine. (For Thudichum and Dupré's method, *v. l.c.* 203.)

Sugar in wine. The sugars occurring in must and in wine are dextrose and lævulose. Cane sugar is never naturally present in must, but it is sometimes added, as in the case of champagne, but even then it is rapidly transformed into invert sugar. Glycerin is formed as a product of the sugar by fermentation, 100 parts of cane sugar or 105·26 parts of grape sugar yielding 3·69 parts of glycerin. In some wines—as *e.g.*, Sauternes and sweet Rhine wines—sugar occurs in the form of inosite.

The colouring matters in wine are due to two sources. In white wines—which range from an almost colourless liquid, as champagne, to the deep yellow sherry—the colour is derived from the oxidation of the so-called extractives contained in the juice, which, as was before explained, is separated from the husks as quickly as possible. In red wines the colour (*œnolin*; *œnotannin*) is due to the matter contained in the husks, stalk, and seeds, which is soluble only by the joint action of acid and the alcohol formed during fermentation. This colouring matter, when isolated, dissolves in water or alcohol with a faint greyish tinge, which, on adding a trace of an acid, assumes a bright-red colour. When exposed to the air, it takes up oxygen, especially when heated, the compound becoming darker and more and more insoluble, and remaining on evaporation as an opaque coating, which dries up to scales. It is still soluble in alcohol, with a purple colour. On adding water the solution remains clear at first, and a precipitate is slowly formed; quickly, however, when a trace of an acid is added. The dried precipitate forms a hard amorphous mass, having a metallic reflection. On heating the powder with a little concentrated potash, it first turns green, then red, and, after a few moments, it dissolves. Acids precipitate from the alkaline solution a gelatinous mass, which is soluble in alcohol and re-precipitated by acids (E. Duclaux, C. R. 78, 1159). The colouring matter of wine may be estimated with sufficient accuracy for technological purposes by precipitating the wine with neutral lead acetate, decomposing the precipitate with sulphuric acid, and titrating the acid solution with potassium permanganate. One part of permanganate corresponds to 1·5 of œnolin (E. Grassi, G. 4,266; C. J. Abst. 1875, 484). By this process, wine is found to contain 35 to 90 centigrams of colouring matter per litre; but the method is open to the objection that the colouring matter, dried at 100°, taken as the standard, may be already partially oxidised. Moreover, the operation being performed on 5 to 10 c.c. of wine, the errors are exaggerated 100 to 200 times in the results given per litre (C. J. Abst. 1874, 716). Some additional amount of tannin is also imparted to wine by the oak of the casks during maturing. Caramel is added to some wines—*e.g.* brown sherry. The grapes of some of the best red wines yield an almost colourless juice if pressed before fermentation, and it is only by the action of fermentation upon the marc that the colour is extracted from it. Mulder separated the colouring matter contained in red wines by means of lead acetate, and found it to consist of a substance which was bluish black in colour and amorphous in structure. It is only sparingly soluble in alcohol, insoluble in water, ether, chloroform, carbon bisulphide, oil of turpentine, oil of olives; but soluble in solution of tartaric acid or cream of tartar, and in alcohol containing a trace of acetic acid, the saturated solution showing a blue colour; more acetic acid turns the solution red. It is soluble also in alcohol containing tartaric acid, exhibiting a red colour, but neither of these acids renders it soluble in ether or chloroform. The colour of wine, consequently, depends both upon the amount of colouring matter and the amount of free acid contained in it, as the violet colour becomes redder in proportion to the quantity of free acid acting upon the blue colouring matter. The colouring matter precipitated by hydrochloric acid—in which it is deposited slowly at the ordinary temperature, but more rapidly on boiling—has been examined by Terreil (Bl. 44, 2). The precipitate always contains a substance resembling ulmic acid, from which the colouring principle may be dissolved out by alcohol. Thus obtained it forms brittle varnish-like scales, insoluble in water and ether, but readily soluble in alcohol, forming a brownish-red solution with a slightly yellow tinge. Acids change this colour to an intense red, while alkalis give a green colouration, which changes rapidly to a brownish yellow on exposure to the air (*cf.* O. Griessmayer, D. P. J. 123, 531; C. J. Abst. 1887, 368). The small quantity of ammonia which is present in grape juice, or is formed during fermentation out of the albuminous substances, is for the most part precipitated during fermentation as magnesium-ammonium phosphate; a small amount, however, remains, and in some wines is accompanied by minute traces of trimethylamine—the amount varies from ·0057 to ·0113 p.c. (Kilicsan).

The albuminous substances in the grape, which set up the ferment, ought by that action to be removed in the yeast when the fermentation is properly carried out. In imperfectly fermented wines a certain amount remains, and, in the case of white wines, may again render them liable to fresh fermentation. In red wines this danger is obviated by the presence of the tannin of the husks, which preserves the albuminous matter from change.

The so-called *extractives* which remain after the extraction of the total solid constituents are characteristic of their origin, and contribute to the smell and taste of wine. Their composition is still very obscure.

The **inorganic substances** contained in wine are potash, soda, lime, magnesia, in combination occasionally with phosphoric and hydrochloric acids. Sherries contain potassium sulphate in excess, owing to the practice of adding gypsum to the must. As regards the amount of alcohol, a very comprehensive set of tables, embracing the results of the examination of 133 wines, is given by Thudichum and Dupré (Treatise on the Origin, Nature, and Varieties of Wine, 281–304), from which the following *résumé* is compiled:—

—	Sp.gr. of wines 1	Sp.gr. minus alcohol 2	Sp.gr. of distillate		Percentage of alcohol by weight in volume		Strength of wines in degree of proof spirit 7
			Found 3	Calculated 4	According to Col. 3 5	According to Col. 4 6	
German wines (excluding one abnormal sample), 35 samples . . .	991·26 to 1000·24	1007·45 to 1014·58	981·36 to 987·49	981·90 to 987·77	11·88 to 7·35	11·47 to 7·17	16·2 to 26·3
French wines, 22 samples	989·34 to 1027·00	1006·34 to 1040·89	974·73 to 985·93	975·05 to 986·71	17·05 to 8·41	16·81 to 7·88	18·0 to 37·2
Spanish wines, 22 samples	985·98 to 1004·74	1009·34 to 1029·97	972·54 to 981·05	972·60 to 981·21	18·77 to 12·11	18·71 to 12·00	26·7 to 41·7
Sicilian wines, 6 samples .	994·11 to 1001·34	1018·56 to 1025·36	975·41 to 975·68	975·45 to 975·98	16·50 to 16·27	16·55 to 16·03	33·5 to 36·3
Portuguese wines, 14 samples	986·95 to 1008·43	1010·24 to 1033·19	971·86 to 983·98	971·90 to 984·95	19·24 to 9·78	19·20 to 9·09	21·9 to 42·5
Hungarian wines, 10 samples	989·42 to 994·27	1006·80 to 1010·88	981·27 to 985·52	981·35 to 982·98	11·96 to 11·05	11·89 to 10·68	19·2 to 26·4
Greek wines, 8 samples .	992·25 to 1113·53	1011·02 to 1126·84	979·04 to 986·45	979·30 to 986·69	13·60 to 8·06	13·41 to 7·91	17·8 to 32·1
Cape wines, 7 samples .	991·03 to 1013·52	1018·87 to 1038·09	966·22 to 975·57	966·29 to 976·36	22·36 to 16·36	22·31 to 15·72	36·1 to 51·7
Atlantic Islands, 3 samples	993·94 to 997·10	1018·95 to 1022·90	973·94 to 974·44	974·20 to 974·99	17·66 to 17·30	17·44 to 16·81	38·2 to 39·1
Elba wines, 1 sample . .	993·02	1016·72	976·40	976·30	15·70	15·80	34·9
Australian wines, 5 samples	985·05 to 1018·86	1006·95 to 1045·00	973·53 to 983·09	973·86 to 983·90	17·99 to 10·62	17·73 to 10·03	23·5 to 40·1

The following analyses of pure wines by R. Fresenius and E. Borgmann (Fr. 22, 46) are also of interest:

Analyses of wines.
(100 c.c. contain grams.)

—		Red Main Wines	White Main	Hocks	White French	Red French	Moselle
Alcohol . .	Maximum	9·51	10·15	10·39	9·84	9·32	8·72
	Minimum	9·49	8·90	6·42	9·05	7·99	7·04
	Average	9·50	9·52	8·77	9·44	8·56	8·08
Extractives .	Maximum	3·30	2·78	3·00	2·62	2·67	2·44
	Minimum	2·70	2·16	1·86	2·47	2·17	1·92
	Average	3·00	2·43	2·32	2·54	2·44	2·11
Mineral matter.	Maximum	0·35	0·20	0·30	0·28	0·27	0·20
	Minimum	0·29	0·17	0·16	0·24	0·21	0·15
	Average	0·32	0·19	0·22	0·26	0·25	0·18
Acidity . .	Maximum	0·62	0·80	0·01	0·71	0·58	0·95
	Minimum	0·54	0·54	0·48	0·54	0·48	0·64
	Average	0·58	0·69	0·66	0·62	0·54	0·79
Glycerin . .	Maximum	1·23	1·34	1·28	1·00	0·99	0·85
	Minimum	1·16	0·86	0·64	0·88	0·75	0·66
	Average	1·19	1·10	0·92	0·94	0·86	0·73
Sulphuric acid .	Maximum	0·082	0·069	0·050	0·019	0·027	0·018
	Minimum	0·070	0·027	0·045	0·015	0·006	0·006
	Average	0·076	0·044	0·047	0·017	0·013	0·012
Phosphoric acid	Maximum	0·065	0·057	0·048	0·046	0·037	0·056
	Minimum	0·065	0·033	0·026	0·023	0·023	0·039
	Average	0·065	0·039	0·040	0·034	0·027	0·047

The mutual relations of the different constituents are on the average as follows:

Alcohol : glycerin . . . = 100 : 10·5
Extract : acidity . . . = 1000 : 16·6
Acidity : mineral matters . = 10 : 3·4
Mineral matters : extractives . = 1 : 11·2
Phosphoric acid : min. matters = 1 : 6·8

Sugar solution wines. The possibility of increasing the quantity of fermentable extract from a given quantity of grapes by the addition of sugar and water seems to have been first suggested by Chaptal. The process in France was worked out by Petiot in 1852. It consisted in adding to the juice before it has time to ferment an equal quantity of sugar solution containing the same amount of sugar as the original must. A similar process, known as 'Gallising,' from its inventor Gall, is also practised in Germany. The must of bad years, which contains a deficiency of sugar and an excess of acid, is mixed with sugar, preferably cane sugar, so as to bring the amount of sugar in the liquid to about 20 p.c., and to reduce the amount of acid to about 2 p.c. Frequently, however, an impure dextrose made from potato or maize starch is used; this addition can frequently be detected in the finished product by its power of turning the plane of polarisation to the right.

The acidity of natural wine can be reduced, as suggested by Liebig, by the addition of neutral potassium tartrate, which throws down the free acid, if present as tartaric acid, as acid potassium tartrate. Wine deficient in alcohol and containing much acid may often be improved by adding to it the pressed residue of a succeeding vintage (*cf.* J. Nessler, B. C. 1884).

A considerable quantity of wine is now made by covering the marc with an aqueous solution of sugar, and allowing the mixture to ferment. The sugar solution contains 18 grms. per litre for every degree of alcohol which it is desired to obtain, and 250 grms. of marc are used for each litre of solution. Analyses of wines prepared in this way by Girard, and of other samples found in commerce, prove that these wines have an approximately definite composition. When they contain from 9 to 10 degrees of alcohol, the proportion of soluble matter, cream of tartar, tannin, and colouring matter is much less than in the ordinary vintage wines. The amount of solid matter varies from 14 to 18 grms. per litre; the amount of cream of tartar is about 2 grms., but not less than 1·6 grm. per litre; whilst the proportion of tannin and colouring matter varies considerably with the nature of the marc. No advantage is gained by allowing the liquid to remain in contact with the marc after fermentation has ceased; on the contrary, the proportion of solid matter, &c., is diminished. No advantage is gained by increasing the proportion of the marc per litre of sugar solution, but the amount of colouring matter and tannin is considerably increased by mixing the marc with the stalks of the grapes. Girard concludes that those wines constitute a highly useful beverage, and can be produced at a very low cost (A. Girard, C. R. 95, 227; C. J. Abst. 1882, 1335).

Plastering of wine. The practice of adding gypsum or plaster of Paris to must, either before or after fermentation, which prevails in Spain, Portugal, and the South of France, is said to have for its object the reduction of the amount of the water in the juice, and the production, consequently, of a must relatively richer in sugar. The fermentation is much more rapid and complete, and it is alleged that the wine keeps longer when it has been plastered, and that the colour is richer and more lasting. This explanation leaves something to be desired, because the sacrifice of other constituents of juice than water by the absorption of plaster is entirely out of proportion to any gain by the absorption of the water, and the result desired could be attained either by the addition of 2 p.c. of sugar or the evaporation of about 11 p.c. of water. The action of the calcium sulphate on the bitartrate of potash in ordinary wine produces an acid sulphate of potash, which gradually forms the normal salt by decomposition of the phosphate present, forming free phosphoric acid, and in wine treated with lime sulphuric acid in a free state and magnesium sulphate. Hence a plastered wine is relatively rich in potash and sulphuric acid. Plastering also decomposes the neutral organic potassium compounds existing in the juice of the grape. The Academy of Medicine of Limoges instituted a lengthened inquiry on this subject in 1888, and reported unfavourably on the effects of plastered wine upon health. It is probable that the reason of the practice, although unknown to those who employ it, is that gypsum precipitates some albuminous matters which injuriously affect the wine. On the other hand, the attempts to deplaster wine are, from a hygienic point of view, more injurious than the plastering, owing to the use of poisonous barium and strontium salts. Plastering is said to modify the chemical characters of the colouring matter of the wine (*cf.* P. Carles, J. Ph. [5] 6, 118).

The Government of the Canton Berne having passed a law forbidding the sale of wines containing more than 2 grms. of potassium sulphate to the litre, wine merchants complained of the severity of the regulation, and the Government appointed a Commission to investigate the subject. Nencki was the reporter, and gives the results of their investigations (J. pr. [2] 25, 284). Opinions were invited as to whether the use of wine containing more than the legal limit of the sulphate is injurious to health; whether the limit could safely be extended, and to what extent; and whether there is any difference between the effects of plastered white and red wines.

Public opinion is strongly against the custom. Spanish, Italian, and South of France wines are those most generally clarified with gypsum. It is said to increase the quantity, improve the colour, and raise the alcoholic strength, thereby improving the keeping qualities; it is also said to prevent after-fermentation. But its real advantage to the wine-maker is that it clarifies the wine rapidly, and allows it to be quickly brought to market. It is chiefly employed with the coarser qualities of red wine, and is either added to the grapes and trodden with them, or, in fewer cases, added to the expressed juice. The quantity used is generally 1–2 kilos. to every 100 kilos. of fruit, but it is sometimes as much as 10 kilos.

The most exhaustive inquiry yet made on the hygienic aspect of the subject was by a Commission appointed by the French War Department, and the conclusions arrived at by them have been confirmed by Nencki and his colleagues. The addition of gypsum to wine cannot be detected by the flavour, but it lessens the intensity of the colour; it decomposes the acid potassium tartrate naturally present in the wine, potassium sulphate remaining in solution and the tartaric acid uniting with the lime to form an insoluble calcium tartrate. Potassium phosphate, also a natural constituent of wine, is decomposed, forming potassium sulphate and insoluble calcium phosphate. It is a debatable question whether the potassium tartrate naturally existing in wine is the acid or neutral salt, and considering that there are also present succinic, malic, and various volatile fatty acids, it is difficult to understand the reactions. But as the natural acidity of wine is more than sufficient to transform all neutral into acid salts, Nencki is of opinion that it is the acid tartrate which is present. It would also appear that some free sulphuric acid is formed in the plastered wine, as when it is left for a certain time ethyl ether is produced; at least, such was the result of one experiment made by Nencki.

Although much has been said as to the baneful effects of plastered wine, very few trustworthy cases have been recorded. The first complaints were made by the French army in Africa, where many cases of illness were said to be caused by its use. The only other attested case is that of an epidemic which broke out in the Department of the Loire, but alum was found to have been added to the wine as well as gypsum. The symptoms are said to be colic, and slight vomiting. The acid potassium tartrate acts towards many reagents in the same manner as free sulphuric acid, and when introduced into the system may have the effect of reducing the alkalinity of the blood.

In view of the inconclusive nature of the evidence, the Commission recommended the maintenance of the regulation forbidding the sale of wines containing more than two grms. of potassium sulphate in the litre (C. J. Abst. 1882, 1248).

According to Griessmayer, when gypsum is added to the must, it forms, with the tartar present, neutral calcium sulphate and free tartaric acid, which latter reacts on the sulphate, forming bitartrate and acid calcium sulphate. The ash of such wine is neutral, and does not give off carbonic acid when treated with hydrochloric acid. When gypsum is added to the finished wine, the alcohol prevents its solution, but it carries down many impurities. Kaiser (B. C. 1881, 632) made experiments to test the value of these conclusions. He found that the calcium bitartrate became bisulphate, and the total tartaric acid became insoluble as a neutral calcium tartrate. In the finished wine, by the addition of gypsum, the tartaric acid is replaced by sulphuric acid, and there is a perceptible increase in the calcium; the other contents remain unaltered. From the proportions of the ash to the extractive matter, Kaiser states that it is possible to declare with certainty whether the wine has been plastered as must or as finished wine; in the first case the ash is disproportionately high, in the other it remains normal.

As to the question whether a plastered wine should be called adulterated, it may be contended that a product which, by treatment, is deprived of its most characteristic constituent, tartaric acid, whilst another substance, calcium sulphate, not normally present, is introduced, cannot be called anything but adulterated.

Wine is liable to be affected by a number of injurious ferments, and is especially subject to acetous fermentation. The action of foreign ferments may frequently be prevented by the process devised by Pasteur, which consists in heating the wine for some time to about 70° in absence of air. The bouquet, and in some cases the colour, is thus found to be improved. The heating must be quickly performed, and, as far as possible, out of contact with air.

As regards the preservation of wine by means of salicylic acid, D. Denucé (C. C. 1882, 265) states that the addition of 10–40 grms. of salicylic acid to 1 hectolitre of pure wine is not injurious to health. It is useless to exceed this quantity, as larger additions of acid would be detected by the taste.

Manufacture of effervescing wines. The effervescence of a sparkling wine is due to the presence of carbonic acid, produced by the fermentation of added sugar. The chief wines of this class (champagne) are produced in the departments of Marne and Haute Marne, and in the vicinity of the Moselle and the Rhine. Both white and red grapes are used, and the wine is amber in colour, the depth of tint depending on the vintage and the proportion of dark grapes employed. The vintage is in the early part of October, and in the pressing the must is separated into two portions, that first produced being of the higher quality. The young wine is allowed to ferment until the winter, when it is racked, and after the expiration of a month the operation is repeated, when the wine is fined. It is then mixed with a certain proportion of old wine, and the amount present determined. If necessary, a quantity of cane sugar is added, and the wine is bottled, the bottles being placed horizontally in piles and left at rest throughout the summer. Carbonic acid is formed, together with a quantity of sediment. When required for the market, the bottles are first carefully brought into an inclined position, so as to cause the sedimentary matter to gradually fall on to the cork; on removing the clip which holds the cork within the neck the pressure of the dissolved gas forces out the cork, together with the sediment. A certain amount (from 1 to 4 p.c., depending upon the sweetness desired) of liqueur, made of fine wine, sugar, and cognac or a still spirit, is quickly added, and the bottles are again filled up, corked, and wired.

Dry champagnes—*i.e.* containing relatively little sugar—are mainly exported to this country, the sweeter varieties being usually consumed on the Continent. The pressure of the dissolved carbonic acid ranges from 5 atmospheres in *grand mousseux* to less than 4 atmospheres in *crémant* wine; in ordinary *mousseux* wine the pressure varies between 4 and $4\frac{1}{2}$ atmospheres.

Wines of France. The chief wine-growing district in France is the Gironde, which is practically divided into five portions, viz., the Médoc, the Graves, the Côtes, the Palus, and the Entre-deux-Mers. In the Médoc some six or seven different varieties of wine are cultivated. Most of the red wine is obtained from the Carbenet Sauvignon, Franc Carbenet, Malbec, and Merlot grapes. The vintage usually begins towards the end of September, and lasts about a fortnight. The wines are divided into *paysan*, *artisan*, *bourgeois*, and *fine growths*, the last group being further subdivided into what are known as 'classed growths,' which, with the communes in which they are produced, are as follows:—

First Growths.

Château Lafitte, Pauillac.
,, Margaux, Margaux.
,, Latour, Pauillac.
,, Haut-Brion, Pessac.

Second Growths.

Château Mouton Rothschild, Pauillac.
,, Rauzan-Ségla, Margaux.
,, Rauzan-Gassies, ,,
,, Léoville-Lascases, St. Julien.
,, Léoville-Poyferré, ,,
,, Léoville-Barton, ,,
,, Durfort-Vivens, Margaux.
,, Lascombes, ,,
,, Gruand-Larose-Sarget, St. Julien.
,, Gruand-Larose, ,,
,, Branne-Cantenac, Cantenac.
,, Pichon-Lougueville-Lalande, Pauillac.
,, Ducru-Beaucaillon, St. Julien.
Cos d'Estournel, St. Estèphe.
Château Montrose.

Third Growths.

Château Kirwan, Cantenac.
,, D'Issan, Cantenac.
,, Lagrange, St. Julien.
,, Langoa, ,,
,, Giscours, Labarde.
,, Malescot, Margaux.
,, Brown Cantenac, Cantenac.
,, Palmer, Cantenac.
,, La Lagune, Ludon.
,, Desmirail, Margaux.
,, Calon-Ségur, St. Estèphe.
,, Ferrière, Margaux.
,, Becker, ,,

Fourth Growths.

Château St. Pierre, St. Julien.
,, Branaire-Duluc, ,,
,, Talbot, ,,
,, Duhart-Millon, Pauillac.
,, Poujet, Cantenac.
,, La Tour Carnet, St. Laurent.
,, Rochet, St. Estèphe.
,, Beychevelle, St. Julien.
Le Prieuré, Cantenac.
Marquis de Therme, Margaux.

Fifth Growths.

Château Poulet-Canet, Pauillac.
,, Batailley, ,,
Grand Pay-Lacoste, ,,
Ducasse-Grand-Pay, ,,
Château Lynch-Bages, ,,
,, Lynch-Moussas, ,,
,, Dauzac, Labarde.
,, Mouton-d'Armailhacq, Pauillac.
,, Le Tertre, Arsac.
,, Haut Bages, Pauillac.
,, Pedesclaux, ,,
,, Belgrave, St. Laurent.
,, Camensac, ,,
Cos-Labory, St. Estèphe.
Château Clerc-Milon, Pauillac.
,, Croizet-Bages, ,,
,, Cantemerle, Macan.

The yield of the whole of these growths has been estimated at about 5,000,000 bottles, from which we gain some idea of the extent of the substitution of 'clarets' which Bordeaux produces. The first-class wines are seldom drunk in France, but are mainly exported to England.

The total amount of land under vine cultivation in the Gironde is about 500,000 acres. During the last twenty years the vineyards have been greatly ravaged by *oïdium* and *phylloxera*, and latterly by mildew, and in parts by *coulure*.

The chief white wine producing district is to the south of Bordeaux. The principal vines are the Semillon, Sauvignon, and Muscatelle. The vintage is much later than in the Médoc—viz. in the last weeks of October or early part of November, when the grapes have entirely ripened. Three qualities of must are produced: the first and ripest juice yields a sweet luscious wine (*vin de tête*), mainly consumed in Russia; the second forms *vin de milieu*, the wine usually known as Sauterne; the third quality, or *queue*, yields a dry white wine. The finer growths are classed as follows:—

Grand First Growth.

Château Yquem, Sauternes.

First Growths.

Château La Tour Blanche, Bommes.
,, Peyraguey, ,,
,, Vigneau, ,,
,, Suduirant, Preignac.
,, Coutet, Barsac.
,, Climens, ,,
,, Bayle, Sauternes.
,, Rieussec, Fargues.
,, Rabant, Bommes.

Second Growths.

Château Myrat, Barsac.
,, Doisy, ,,
,, Peyxotto, Bommes.
,, D'Arche, Sauternes.
,, Filhot, ,,
,, Bronstet-Nérac, Barsac.
,, Caillou, ,,
,, Suau, ,,
,, Malle, Preignac.
,, Romer, ,,
,, Lamothe, Sauternes.

The department of the Pyrénées Orientales produces a considerable quantity of wine, mostly from the Grenache noir and Carignane grapes. The generic name of the wine of the district is Roussillon, of which the most esteemed varieties are muscat of Rivesaltes, Maccabeo, Grenache, and Malvoisie, which are liqueur wines; and Rancios, dry Malvoisie, and Picfoule. Languedoc also produces a large quantity of wine (*vins du Midi*), much of which is mixed with the wines of the Gironde and of Burgundy; whilst a considerable amount of the rest is distilled to make 'trois-six' and *eau de vie*.

The Rhône and Saône valleys produce the chief wines of the east of France, which, with the exception of Hermitage and the wines of the Beaujolais, seldom occur in trade under their own names.

The best qualities of champagne are produced in the departments of Marne and Haute-Marne, the chief centres of the trade being at Rheims, Épernay, Aÿ, Avize, Châlons, and Dizy. Large quantities of sparkling wine are produced in the Saumur, in the department of Maine-et-Loire. Sparkling Saumur is made from both black and white grapes—the black being the product of the Breton vine, the white that of the Pineau blanc. The wine is made much in the same way as champagne, except that, as a rule, the finished product is a mixture of two successive vintages.

The wines of Burgundy are produced in the departments of Côte-d'Or, Yonne, and Saône-et-Loire. The best growths are classified as follows:—

Red Wines.

Class 1. Romanée-Conti, Chambertin, Clos Vougeot, Richbourg la Tâche.

Class 2. Musigny, Romanée St.-Vivant, Le Clos Saint-Georges, Le Corton, Les Bonnes Mares, Le Clos du Tart.

Class 3. Arvelets, Rugiens, Beaumont, Cailles, Cras-Murge, Boudots, Perrets, Pruliers, Thaurey, Vaucrains, Cailleret Champans, Clavoillon, Clos Margeot, Clos Tavannes Noyer, Bart, Echezaux, Fèves, Grèves, Ferrière Sautenot.

White Wines.

Class 1. Montrachet.

Class 2. Chevalier Montrachet, Batard Montrachet Charmes, Combettes, Genevrières, Goutte d'Or, Charlemagne.

Good red and white wine is also produced in Yonne. The red resembles Burgundy; the white is known as Chablis. Maçon is produced in the department of Saône-et-Loire; it is similar to Burgundy, but is lighter in colour and lacks its body and bouquet. Hermitage is produced in the department of Drôme. Cognac is obtained from wines produced in the departments of Charente and Charente-Inférieure. The manufacture has, however, greatly suffered from the effects of *Phylloxera*, and pure genuine cognac now commands an almost prohibitive price.

Spain. Sherry, the best known of Spanish wines, is mainly produced in Andalusia, and derives its name from Jerez or Xeres de la Frontera, the chief centre of the trade, and where most of the wine is produced from must or fruit purchased from the growers. Sherries are usually broadly classed as Amontillados and Manzanillas. The former are usually deeper in colour and more alcoholic from added spirit; the latter are lighter and dryer, and are, as a rule, shipped unbrandied. Montilla produced in the province of Cordova somewhat resembles Manzanilla. The sweet red wine known as 'tent,' which is used for ecclesiastical purposes, is a summered coloured wine mainly obtained from the Rota district. Large quantities of wine are exported to France from Catalonia and Aragon. Of late years a considerable amount of red wine has been sent to this country from Rioja.

Portugal. Port is mainly the produce of the rugged and mountainous district of the Alto Douro in the north-east of Portugal. The vintage usually begins at the end of September. The grapes, from which the stalks are removed, are emptied into stone tanks holding from seven to thirty pipes, and are pressed, first by treading and then by means of a beam or screw press. After from 48 to 60 hours' treading the must is left to ferment, drawn off into vats, and mixed with a sufficient quantity of alcohol to prevent acetous fermentation. After the lees are deposited the wine is again racked and mixed with more alcohol, which is usually obtained by distilling wine. In the spring it is sent down to Oporto, where it is stored previous to shipment.

Port first appeared in England at about the end of the seventeenth century, and its consumption in this country gradually increased up to the middle of the eighteenth century, when it declined. During recent years the vineyards of the Alto Douro have suffered greatly from *oïdium* and *phylloxera.* At the present time Oporto ships annually about 70,000 pipes of wine, nearly half of which is sent to Great Britain.

The South of Portugal (Torres Vedras and Collares) produces a considerable quantity of a rough kind of claret, and also a white wine known in England as Bucellas Hock, which is obtained from the Riesling grape.

Italy. About 700,000,000 gallons of wine are produced in Italy—more, indeed, than in France—but it is only within the last few years that Italian wines have found much favour in this country. Their consumption will be still further increased now that improved methods of cultivation and manufacture are being more generally employed. Northern Italy produces Montferrat and Asti, together with a certain amount of sparkling wine. Montepulciano, Chianti, Pomino, Montalcino, and Carmignano are made in Central Italy; whilst the Neapolitan district yields Lacryma Christi and a variety of Malvoisie and good class Muscat wines.

Sicily. The chief Sicilian wine is Marsala, which is obtained from a mixture of selected and thoroughly ripe grapes of the Madeira variety. It is carefully manufactured and is very uniform in quality, although, as a rule, somewhat heavily fortified.

F. Sestini and G. Del Torre (L. V. 17, 424) have analysed a number of Italian and Sicilian wines. The percentage of alcohol by volume in these wines varies generally between 13 and 14; in Sicilian wine it reaches in exceptional cases 22 p.c. The mean of 167 red varieties was 13–14 p.c. In one-fourth of the wines the quantity of free acid was 5 to 6 p.c., but in Venetian wines there was a larger quantity. The ratio of volatile acids to fixed acids was rarely 1:2, the average 1:3 in Sicilian wines, and 1:4 in the dry wines of North Italy; however, in many wines of Central Italy the quantity is much greater. Tannin is present in small quantity only; average, about ·05 p.c.

Hungary. Both white and red wines are made in Hungary. It is estimated that there are about 1,000,000 acres of land under vine cultivation in the province, inclusive of Croatia and Slavonia, yielding 250,000,000 gallons annually. The most famous of Hungarian wines is the Sweet Tokay or Essentia, which is made from the first runnings of the ripe grapes obtained without pressure. Only a small portion is so obtained, and it rarely, if ever, appears in the market. Other varieties of Tokay are known as *Ausbruch* and *Mâstâs.* Carlowitz resembles port in character, and is produced on the banks of the Danube, about 40 miles to the north-west of Belgrade.

Excellent red wines, resembling Burgundy, are now made in Dalmatia. The most esteemed varieties are Moscato Roso, Vino Taitaro, Prosecco Vugova, Maraschino, and Malvasia.

Germany. The chief wine-producing districts of Germany are Alsace-Lorraine, Baden, Würtemburg, Hesse, Bavaria, and the Rheingau, which together yield about 80,000,000 gallons. The celebrated Steinberg, Johannisberg, Rüdesheim, Gräfenberg, and Rauenthal wines are produced in the neighbourhood of the Rhine, not far from Mainz, which is the centre of the hock trade. The vineyards of Hesse yield Liebfraumilch, Nierstein, and Scharlachberg; Hochheimer is obtained from the Maingau. The chief Rhine vine is the Riesling, which is said to be indigenous, although the Oesterreicher, Kleinberger, Sylvaner, and Blue Trollinger varieties are common, especially on the lower grounds.

The chief product is a white wine. A certain amount of red wine is obtained, notably Assmannshausen, from Riesling and mixed grapes. The German wine-maker has to struggle with many natural disadvantages, but in no part of the world is the manufacture more intelligently conducted, or, in good seasons, with better results. The Moselle district also produces excellent wines of characteristic flavour and aroma.

The Atlantic Isles. Grand Canary and Teneriffe produce a small quantity of wine, but the yield has been hitherto limited owing to the attacks of *oïdium.* Since the production of cochineal has fallen off on account of the influence of the coal-tar colouring matters, vine culture is being resumed, and wines of the Madeira type are being made in larger quantity.

Madeira formerly shipped comparatively large quantities of wine to England, as much as 520,000 gallons being imported in 1820. The trade subsequently declined, partly through a change in fashion and partly from the devastation caused by *oïdium.* The vineyards are now being replanted, and an increasing amount is gradually making its way to this country. The best-known varieties are Malmsey, Sercial, Bual, and Tinta. The characteristic flavour of Madeira is probably due to the practice of heating the wine shortly after its manufacture to a temperature varying from 25° to 45°. Formerly the same condition was obtained by sending the wine a voyage to the East or West Indies and back.

A small quantity of wine is made in the Azores, particularly on Pico, but it is of very indifferent quality, and is mainly exported as low-class sherry.

Cape of Good Hope. Comparatively little wine is now sent to this country from South Africa, principally owing to the alteration of the wine duties of 1860.

Australia. Of late years a considerable amount of wine from Victoria, New South Wales, and South Australia has been imported into this country, and the produce of the vineyards of Highercombe, Tintara, and Auldana appears to be steadily increasing in popular favour.

United States. The manufacture of wine is now firmly established in California. The produce was originally derived from the 'Mission' grape, supposed to have been imported from Mexico by Franciscan monks, but German, French, and Spanish varieties have now been introduced, and wines in some degree resembling those of these countries are now made on a considerable scale. The vine is also cultivated on a large scale in Ohio, and clarets and champagnes are made in the vicinity of Cleveland and Sandusky. Other wine-producing States are New York, Missouri, Illinois, and Pennsylvania. The principal grapes in the eastern and central States are the Catawba and the Ives Seedling; in the Southern States the Scuppernong and Virginia Seedling are most frequent. The imports of foreign wines into the United States have steadily diminished during the last twenty years. The total annual production in the United States is estimated at about 40,000,000 gallons.

The following analyses, by R. M. Cooper (C. N. 32, 160), of twelve samples of wines manufactured in Virginia from grapes grown in that State are of interest as showing the general chemical character of American wines: —

No.	Name	Source	Description	Specific gravity	Alcohol	Ash
1	Virginia Claret .	Alvey grape .	Red, without addition .	0·9949	9·80	0·24
2	Virginia Hock .	Concord grape .	White, without addition .	0·9932	8·56	0·17
3	Bacchantees .	Concord grape .	Light red, 1871 . . .	0·9941	10·04	0·14
4	Concord . . .	Concord grape .	Medium red	0·9926	10·03	0·15
5	Sweet Concord .	Concord grape .	Deep red, syrup added .	1·0050	11·79	0·13
6	Ives	Ives grape . .	Red, from pure juice . .	0·9913	11·13	0·12
7	Delaware . . .	Delaware grape	White, sugar added . .	0·9931	9·46	0·24
8	Sweet Delaware	Delaware grape	White, syrup added . .	1·0117	10·57	0·17
9	Delaware . . .	Delaware grape	White, from pure juice .	0·9875	12·69	0·12
10	Calawaba . . .	Calawaba grape	White, from pure juice .	0·9902	10·04	0·13
11	Norton's . . .	Norton's Virginia grape .	Purple red, no addition .	0·9953	10·57	0·31
12	Dry Norton's Virginia . . .	Norton's Virginia grape .	Deep red	0·9981	11·79	0·20

No.	Volatile acid	Non-volatile acid	Sugar (glucose)	Tannic acid	Potassium carbonate	Total solid residue	Nitrogen
1	0·15	0·60	0·70	0·018	0·148	1·78	0·013
2	0·07	0·43	0·058	0·004	0·111	1·84	0·019
3	0·15	0·35	0·047	0·019	0·098	1·52	0·013
4	0·13	0·44	0·045	0·011	0·098	1·60	0·006
5	0·39	0·17	3·152	0·006	0·111	5·11	0·006
6	0·12	0·57	0·065	0·009	0·074	1·69	0·008
7	0·10	0·41	0·075	0·008	0·160	1·98	0·014
8	0·56	0·01	3·703	0·006	0·111	6·41	0·009
9	0·08	0·41	0·106	0·002	0·086	1·42	0·016
10	0·16	0·42	0·031	0·003	0·086	1·41	0·012
11	0·22	0·48	0·112	0·019	0·234	2·66	0·018
12	0·41	0·50	1·228	0·001	0·148	2·55	0·016

ANALYSIS OF WINE.

The chemical examination of wine is usually restricted to the determination of those constituents which enable an opinion to be formed concerning its purity or freedom from adulteration (*cf.* W. Fresenius and Haas, Fr. 30, 499).

1. For the estimation of the *specific gravity* a determination by the bottle at 15°C. is to serve as the basis; it must be given accurately to four decimal places.

2. The results should be given in grms. per 100 c.c. or per litre. Koenig (Fr. 28, 202), however, deprecates this practice, on the ground that for sweet wines, which are liable to differ widely in sp. gr., the results are no longer directly comparable.

3. The *alcohol* is to be determined by the distillation method, the sp.gr. of the weighed distillate is taken with the bottle at 15°, and the proportion of alcohol calculated therefrom.

4. *Determination of extract*: (*a*) Of wines with an extract amounting to 3 grms. per 100 c.c., 50 c.c. are evaporated in a flat-bottomed platinum capsule upon the water-bath; the residue is heated two and a half hours in the steam oven, and finally cooled in the desiccator and weighed. The German Imperial Commission of 1884 have prescribed the following method: 50 c.c., measured at 15°, are evaporated on the water-bath in a platinum basin of 85 mm. diameter, 20 mm. height, and 75 c.c. capacity, and the residue is dried for two and a half hours in the water oven. For sweet wines an amount yielding from 1 to 1·5 grm. of residue is taken. For the necessity of using dishes of similar area and surface in order to obtain comparable results *v.* Bouilhon (C. R. 103, 498).

(*b*) Wines containing a higher proportion of extract are to be diluted with water, so as not to contain more than 3 grms. extract in 100 c.c. The residue is to be treated as above.

(*c*) For sweet wines the indirect method of determining the extract from the sp.gr. of the wine after removal of the alcohol is to be preferred.

Estimation of alcohol and extractive matter in wine (H. Hager, C. C. 1878, 415). The sp.gr. of the wine is determined: 100 c.c. are evaporated to about a third of the original volume, the residual liquid is diluted with water to 100 c.c., and the sp.gr. is again determined. The difference between the two numbers deducted from 1,000 gives the sp.gr. of dilute alcohol equal in strength to the original wine; from this, the amount of alcohol is found by the use of tables. From the second sp.gr. determination (that of the aqueous extract) the percentage amount of extractive matter may be found by the aid of the following table, which is based upon Hager's experiments.

Temperature = 15°. The sp.gr. increases or diminishes by 0·00024 for each degree C.

P.c. of extractive	Sp.gr.	P.c. of extractive	Sp.gr.
0·50	1·0022	7·50	1·0343
0·75	1·0034	7·75	1·0355
1·00	1·0046	8·00	1·0367
1·25	1·0057	8·25	1·0378
1·50	1·0068	8·50	1·0390
1·75	1·0079	8·75	1·0402
2·00	1·0091	9·00	1·0414
2·25	1·0102	9·25	1·0426
2·50	1·0114	9·50	1·0437
2·75	1·0125	9·75	1·0449
3·00	1·0137	10·00	1·0461
3·25	1·0148	10·25	1·0473
3·50	1·0160	10·50	1·0485
3·75	1·0171	10·75	1·0496
4·00	1·0183	11·00	1·0508
4·25	1·0194	11·25	1·0520
4·50	1·0205	11·50	1·0532
4·75	1·0216	11·75	1·0544
5·00	1·0228	12·00	1·0555
5·25	1·0239	12·25	1·0567
5·50	1·0257	12·50	1·0579
5·75	1·0263	12·75	1·0591
6·00	1·0274	13·00	1·0603
6·25	1·0286	13·25	1·0614
6·50	1·0298	13·50	1·0626
6·75	1·0309	13·75	1·0638
7·00	1·0321	14·00	1·0657
7·25	1·0332	14·25	1·0663

(C. J. 1879, 179).

For more recent tables see Schultz, Fr. 19, 104. According to Haas, the indirect method is applicable only to sweet wines, since in fully fermented wines the assumption on which the tables have been constructed—that the solutions of the extractive matters have the same sp.gr. as that of sugar—is incorrect. E. H. Amagat (C. R. 99, 195) boils the wine until its volume is reduced one half, in order to expel alcohol; and the original volume is then restored by addition of water, and the sp.gr. determined. The amount of dry extract is very nearly, although not exactly, proportional to the difference between its sp.gr. and unity.

In completely fermented wines the amount of extract is seldom less than 14 grms. per litre. Wines containing less than this amount after removal of the sugar may be suspected, unless it can be shown that natural wines from the same district, and this vintage, actually contain so small an amount of extract.

After separation of the non-volatile acids, the remaining extract in natural wine is seldom less than 11 grms. per litre, and after separation of the free acids, as a rule, not less than 10 grms. per litre.

According to Portele, when red wine is cleared with gelatin the percentage of extract is considerably reduced, so that really good natural wines may be reduced below the minimum, ·65 p.c. of solid extract. The clearing of wine by gelatin has a considerable effect on the colour of inferior qualities, some of these being quite decolourised (K. Portele, B. C. 1884, 57; C. J. Abst. 1884, 938).

A. Gautier (Bl. [2] 27, 7) has studied the influence of dilution, plastering, brandying, &c., on the weight of the dry extract. When skilfully done, it is generally very difficult to detect the addition of water to wine naturally rich in alcohol for the purpose of fraudulent adulteration. Generally, the expert founds his judgment on the low percentage of dry extract and of glycerin, but grave sources of error may creep in if care be not taken.

In the determination of the extract, the evaporation of the wine at 100° and drying the residue on the air-bath may give inaccurate results owing to loss of glycerin &c., and to the alteration of the tannin and nitrogenous matters. These sources of error, however, are entirely avoided by evaporating to dryness and drying in a vacuum for several days at the ordinary temperature—no alteration taking place after ninety-six hours at 25–32°. As might be expected, the results thus obtained are always higher than those obtained by the ordinary method (*v.* Magnier de la Source, Bl. [2] 26, 488). The influence of plastering on wine is to raise the amount of extract by about 3·0 to 3·8 grms. per litre, the Vins du Midi being raised from 18·2 grms. extract per litre to 21·5 to 23·8 grms. The effect of fining on the weight of the dry extract is to diminish it, whether gelatin or white of egg be employed, since the tannin becomes precipitated; and brandying has the same effect, not only because it increases the volume of the wine without adding any solid material, but also because it precipitates, after a time, certain substances dissolved in the wine, especially the acid potassic tartrate. The stoppage of the fermentation by means of sulphurous acid, alcohol, or salicylic acid retains a portion of the glucose, and so increases the amount of extract. In order, to ascertain whether a wine has been diluted, it is necessary to determine the amount of extract and compare it with wines of the same vintage and same year, having special regard to the amount of tannin and glycerin, and also whether the wine has been plastered, which is easily ascertained by its giving a precipitate with barium chloride, and by the ash being neutral if it has not been mixed with unplastered wines. If the proportion of glycerin is small, whilst the extract is normal, it is probable that the wine has been diluted with washings of the marc from which the wine was made, as this would introduce appreciable quantities of colouring matter, cream of tartar and tannin (C. J. Abst. 1877, 750).

According to E. Hondart (Bl. [2] 28, 59), a certain relation exists between the density of a wine and the weights of water, alcohol, and extract which it contains, and upon this relation two methods may be based for the determination of the extract.

(*a*) The alcohol is distilled from the wine, and the residue filled up with distilled water to its original volume; the density of the liquid is then taken to three places of decimals, the last two of which multiplied by 2·25 give the weight of the extract. As this method requires great practice before accurate results can be obtained, the following, which is of greater practical use, has been devised.

(*b*) The alcoholic strength of the wine is ascertained by means of Gay-Lussac's tables. The density of the wine is taken with a *baroneometer* (an instrument constructed for the purpose by Hondart), and the difference between the two densities is multiplied by 2·06, which gives the weight of the extract (C. J. Abst. 1877, 939).

The various methods of determining extractive matter in wine differ not only in the details of manipulation, but also in principle, some chemists including in the term 'extractives' all matters other than water, alcohol, or volatile acids; others only those substances which are not volatile at 100° or 110°C. Thus in the one case the glycerin would be counted among the extractives, but not in the other. Nessler and Barth (Fr. 1882, 43) consider that the glycerin should properly be included among the extractive matters, and they recommend that two separate quantities of wine should be evaporated, the one with addition of a measured amount of titrated baryta water, the other without any addition, the residue obtained in the former case being dried at 110–115° for eight hours; in the latter for four hours at 100° in a current of dry air. The addition of baryta (first recommended by Grete) completely binds the glycerin, the difference between the two sets of determinations being glycerin and volatile acids.

From the results of very numerous analyses, Nessler and Barth conclude that in pure well-fermented wines the proportion of extractives (including glycerin) stands in a certain relation to the total acidity. After subtraction of the latter it never amounts to less than 1 p.c. Strongly alcoholic wines always contain more glycerin than weak wines, the glycerin always amounting from 7 to 10 p.c. of the quantity of alcohol. The mineral constituents usually are about 10 p.c. of the total extract.

5. The *free acid* is determined by titration with standard potash or soda-lye, using litmus-paper as indicator, and calculating the result as tartaric acid ($C_4H_6O_6$). Volatile acids are to be determined by distillation in steam, and to be expressed as acetic acid ($C_2H_4O_2$).

Old wines have an acid reaction, in consequence of the presence of a certain amount of free acid and potassium bi-tartrate. A wine not exhibiting this acid reaction tastes flat; the acidity is its most important flavour. For a long time it has been believed that the free acid of wine is tartaric acid alone. Nessler's researches have, however, shown that this is seldom the case. Tartaric and malic acids often exist together, and more frequently the free acids consist of malic acid entirely. Wines containing tartaric acid alone taste more tart than those with only malic acid, or a mixture of malic and tartaric acids. Nessler shows that only in rare cases does the free acid in grapes consist solely of tartaric acid; in most cases a mixture of malic and tartaric acids is present in variable proportions (Graeger, C. C. 1873, 105; C. J. Abst. 1873, 659).

Detection and estimation of butyric acid in presence of acetic acid. 500 c.c. of wine is distilled until 125 c.c. remains; the residue is diluted to its original bulk, and again distilled until 125 c.c. remains. This is repeated four times, and the free acid in the united distillates determined by titration with soda or with baryta. If soda has been used, the neutralised distillate is evaporated down, treated with dilute sulphuric acid, steam distilled, and the distillate neutralised with baryta. The solution is so far evaporated down that it will solidify when cold, after which it is treated with absolute alcohol (10 parts). The barium butyrate dissolves, whilst the acetate remains almost entirely undissolved. The salts are separated by filtration and washing with absolute alcohol. The aqueous solutions of the salts are treated with sulphuric acid, steam distilled, and the acid determined by titration with soda. In order to ascertain whether the separation was complete, the neutralised solutions are evaporated down and treated with alcohol and sulphuric acid; a trace of impurity is easily detected by the odour of the ethyl salt.

Detection and estimation of lactic acid. 500 c.c. of wine is just neutralised with soda, some pumice powder added, and the whole evaporated to dryness in a deep dish on a water-bath, with frequent stirring. The residue is rubbed in a mortar, moistened with dilute sulphuric acid, and shaken three times with ether (200 c.c.). The united ether extracts are carefully evaporated down in an Erlenmeyer flask, the residue washed with water into a deep dish, treated with an equal volume of alcohol, and slightly heated for a long time with freshly-precipitated lead carbonate, until effervescence ceases. It is then digested for three or four hours, filtered, and washed with 95 p.c. alcohol. The filtrate is decomposed by hydrogen sulphide, filtered, heated on a water-bath to remove excess of hydrogen sulphide, and distilled until one quarter remains. It is then diluted to its original bulk, and again distilled, and this is repeated until the distillate is neutralised by not more than 0·5 c.c. of normal soda solution. The lactic acid in the residue is determined by titration. The results thus obtained are too high, owing to the presence of malic acid. The neutralised solution is therefore evaporated to dryness, and the sodium lactate dissolved out by absolute alcohol (sodium malate being insoluble). After evaporation of the alcohol, the residue is treated with dilute sulphuric acid, and extracted three times with ether. The residue from the ether is digested with lead carbonate, and the acid afterwards liberated as before. The solution of acid is divided into two parts, the one being used for the titration, and the other converted into the zinc salt to determine its purity (C. J. Abst. 1890, 1344).

The presence of free tartaric acid in wine does not necessarily show an improper admixture of tartaric acid with the wine. According to Mach and Rolondi, the amount of free tartaric acid in the grape increases in proportion to the degree of unripeness, so that its absence from wine can only occur under certain conditions of ripeness of the grapes employed. Although unripe grapes are frequently used in considerable quantity in wine-making, yet if the ripe grapes are in excess, the potash salts in them are more than sufficient to separate the free tartaric acid in the form of tartar, and this explains the fact that wine so made generally contains no free tartaric acid. A wine may be suspected of having been sophisticated if, with a small amount of free acid, an undue proportion of it is tartaric (J. Nessler and H. Wachter, B. C. 1880; C. J. Abst. 1880, 775).

6. *The determination of the glycerin* in ordinary wines (not sweet wines) is to be carried out according to the method agreed on by the German or Austrian chemists, without a correction for evaporation. The determination of glycerin in sweet wines does not give accurate results. If required, Borgmann's method is to be preferred. This is as follows: 100 c.c. of the wine are evaporated with sand, the residue is extracted with 100 c.c. of absolute alcohol, the solution is diluted, and then well shaken with 1·5 times its bulk of ether, by which the sugar is mostly precipitated, whilst all the glycerin remains in solution; this is poured off and treated in the usual way.

Reichardt (Ar. Ph. [3] 10, 4080) has simplified Pasteur's method of determining glycerin as follows: The wine extract obtained by evaporation is mixed with slaked lime in slight excess, and evaporated to dryness. On extracting this residue with 90 p.c. alcohol, the succinic acid and sugar remain as insoluble lime compounds, and the alcohol solution, when evaporated on a water-bath, leaves the glycerin in the pure state.

Reichardt states that in the case of wines which contain potato sugar, the glycerin requires to be further treated with a mixture of alcohol and ether, in order to separate from it certain dextrinoid substances whose presence is indicated by the thickening of the impure glycerin on cooling.

Reichardt's numbers are, however, found to be invariably higher than those of Pasteur for pure wines. This Neubauer and Borgmann (Fr. 1878, 442) believe to be due to impurities present in the glycerin, and they further consider that the impurities separated by alcohol-ether as described above could not resemble dextrin, since they exerted no rotatory effect on polarised light. The substances are probably normal constituents of genuine wine, and therefore are always present in the glycerin separated by Reichardt's method. In investigating the matter experimentally, Neubauer and Borgmann first proved that a solution of 2 grms. of glycerin in 10 c.c. of absolute alcohol gave not the faintest turbidity when mixed with 15 c.c. of ether. A great number of genuine wines were then examined by Reichardt's method, but in every analysis the glycerin was subjected to the purification by alcohol-ether, and the weights of glycerin and of impurity estimated. In every case the treatment with alcohol-ether caused the separation of impurities from the glycerin, the weight separated averaging about one-fifth that of the purified glycerin. The glycerin thus obtained was found, however, to be still impure; it yielded on an average over 2 p.c. of ash, evolved ammonia when heated with soda-lime, and was rendered slightly turbid on addition of tannin solution. The nitrogenous substances present were further found to be of different kinds, as after complete precipitation by tannin solution both the precipitate and the filtrate still yielded ammonia when burnt with soda-lime. Of the nature of these azotised bodies we are as yet quite ignorant. Reichardt's method was further tested by applying it to the estimation of pure glycerin, added in known quantity to wines whose natural glycerin had been previously determined with great care. The results thus obtained were satisfactory, the error being *minus*, and seldom reaching one-tenth per cent. when quantities of glycerin varying from 0·6 to 2·5 grms. were added to 100 c.c. of wine. There is no doubt, therefore, that this method would detect the adulteration of a wine with glycerin to any great extent. On the other hand, wines containing only 0·07–0·08 p.c. of glycerin are suspicious, since pure wines usually contain from 0·7–1·2 p.c. as estimated by the above method. Further, wines which yield 16–17 p.c. of alcohol to 0·12 of mineral matter and 0·299 of glycerin are certainly artificial, and are not produced by the fermentation of the juice of the grape.

Bensmann (D. P. J. 261, 404) gives the following process for the estimation of glycerin. 100 c.c. of wine is mixed with 5 grms. of calcium hydroxide in a porcelain dish, and the mixture evaporated nearly to dryness on the water-bath. The residue is then mixed with from 5 to 10 grms. of gypsum to form a stiff mass, and extracted with 50 c.c. of 90 p.c. alcohol in an extraction apparatus. The alcoholic solution is evaporated to a stiff syrupy consistence, and the residue dissolved in 90 p.c. alcohol. The solution is brought into a 50 c.c. cylinder graduated in cubic centimetres, and provided with a glass stopper, treated with 20 c.c. of alcohol (90 per cent.), and made up to 50 c.c. with ether. After settling, 25 c.c. of the solution (corresponding with 50 c.c. of wine) is evaporated to dryness in a flask, dried at 90°, and weighed. The weight, less the ash, represents the amount of glycerin in the wine.

Weigert (C. C. 1888, 1511) recommends the following method: 100 c.c. of wine (dry or sweet) is concentrated on the water-bath to 3–5 c.c., 3–5 grms. of slaked lime is added, and then 50 to 80 c.c. of 90–96 p.c. alcohol, the mixture being then heated on the water-bath until the alcohol has boiled a few minutes. The solution is then filtered, the residue treated a second time with 45–50 c.c. of the alcohol, and the whole brought on to the filter and washed with 50–80 c.c. alcohol. The filtrate is concentrated on the water-bath, preferably in a 250 c.c. flask, to a syrup, 10–20 c.c. of absolute alcohol and 15–30 c.c. of ether added, and after the solution has cleared the ether layer is poured off into the weighing glass. The residue is again treated with a mixture of alcohol (1 part) and ether

($1\frac{1}{2}$ parts), and the extract added to the first. The ether and alcohol are evaporated off, and the glycerin remaining finally weighed.

In the case of sweet wines no lime is employed, but in other respects the procedure is similar. The glycerin should always be tested for sugar. In judging a wine in regard to the proportions subsisting between the glycerin and alcohol, the presence of acetic acid or the addition of salicylic acid, whether the proportion of nitrogen varies much from the average, or whether the wine has been strongly sulphured, should always be taken into account (C. J. 1889, 446; *v.* also Samuelson, C. C. 2, 10, 933; C. J. Abst. 1887, 86; also Barth, C. C. 1886, 504; C. J. Abst. 1887, 184).

Toerring (Zeit. Ang. Chem. 1889, 362) purifies the glycerin by distillation under reduced pressure, and treats the aqueous distillate, which should contain 0·5 to 1 p.c. glycerin, with 5 c.c. benzoic chloride and 35 c.c. of 10 p.c. soda solution, and shakes vigorously. The precipitated glyceryl benzoate is collected on a tared filter, washed with water, dried at 100°, and weighed: 1 part of glycerin gives 3·85 parts of benzoate (C. J. Abst. 1890, 426).

The relation between alcohol and glycerin in natural wines may vary between 100 parts by weight of alcohol to 7 parts by weight of glycerin. From a number of experiments, Borgmann concludes that the proportion of glycerin to alcohol is never less in pure wines than 7·8 to 100 (E. Borgmann, C. R. 22, 58; C. J. Abst. 1883, 518). Wines showing a different relation between spirit and glycerin may be suspected to contain either added alcohol or added glycerin. In natural dry wines the weight of the glycerin is never more than half the amount of the extract after the removal of the sugar.

7. *Mineral matter* is found by incinerating the residue from the evaporation of 50 c.c.

Wine containing less than 1·3 mineral matter per litre may be suspected unless it can be shown that natural wine from the same district and of the same vintage actually contains so small an amount of inorganic matter. The ratio of mineral matter to extract is, as a rule, about 1 to 10.

Estimation of chlorine in wine. It is well known to wine falsifiers that chemists lay much stress on the proportion of mineral matters contained in wine, and therefore they frequently add sodium chloride to artificial or adulterated wines in order to bring the total amount of ash up to the normal quantity. Such wines do not readily yield a white ash, and a notable proportion of chlorine volatilises during the incineration. Hence the determination of the chloride has to be effected in the wine itself, and not in the ash. The ordinary method of chlorine titration with potassium monochromate as an indicator not being applicable, on account of the solubility of silver chromate in the free acid of the wine, and of the obscurity of the end reaction in wines previously neutralised, and Volhard's method likewise giving unsatisfactory results for the reason last mentioned, Nessler and Barth find it necessary to operate as follows:—50 c.c. of the decolourised wine are acidulated with nitric acid, an excess of standard silver solution is added, and then standard thiocyanate solution is run in until a drop of the liquid when mixed on a plate with ferric sulphate solution just shows a pink colouration.

The proportion of chlorine present in genuine wines usually lies between 0·002 and 0·0025 p.c., and never exceeds 0·006 p.c.

Wines containing more than 0·05 p.c. sodium chloride may as a rule be suspected. Exceptions may occur in the case of wines which have been produced in the neighbourhood of the sea-shore.

Alkaline earths in wine. The ashes of wine always contain calcium and magnesium salts. The amount of calcium (3 to 11·4 milligrams in 100 c.c. of wine) is greatest in young wines and gradually diminishes with age, probably in consequence of the separation of neutral calcium tartrate. The amount of magnesium, on the other hand, remains almost constant and is always in excess of the calcium. The largest amount of magnesium found by Kayser was 24 milligrams in 100 c.c. of Malaga wine. The phosphoric acid and magnesia show a constant proportion of 10 : 6, corresponding with the formula $MgHPO_4$ (Kayser, C. C. 1881, 394; C. J. Abst. 1882, 121).

8. Polarisation may often be dispensed with in dry wines; in sweet wines it must be resorted to before and after inversion.

Sugar is to be determined according to the methods of Soxhlet or Allihn, and to be expressed as grape sugar. If the proportion of sugar is considerable, or if the difference between the proportion of extract and the quantity of directly reductive sugar is exceptionally high, a determination of sugar must be carried out after inversion.

The sugar in wine is a variable mixture of dextrose and lævulose, and occasionally saccharose. The usual method of examination consists in estimating the total quantity of sugar by titration with copper solution and then ascertaining by the optical method the proportions of the two glucoses and inverting with hydrochloric acid for the detection of the saccharose. Borntrager (Zeits. Ang. Chem. 1889, 477) considers that in our present ignorance of the true rotatory power and reducing action of lævulose, the exact calculation of the proportions of the sugars has only a relative value. His mode of preparing the wine for examination is as follows: The wine is accurately neutralised in the cold with soda or potash, evaporated on the water-bath until the alcohol is expelled, mixed, after cooling, with a moderate quantity of lead acetate, made up to the original volume, and filtered. After the lapse of twenty-four hours this filtrate is fit for both polariscopic examination and for titration. If, however, the wine is so dark-coloured that the above method only gives a sufficiently colourless filtrate when the amount of acetate is large enough to produce an alkaline reaction, it is necessary to neutralise the filtrate with acetic acid and dilute to double the volume. Although the specific rotatory power of both dextrose and lævulose varies with the strength of the solution, yet within the limits occurring in wines the variations need not be taken into account. The specific rotatory power of lævulose increases, however, so much more rapidly than that of dextrose that in wines containing a great excess of the former little more can be done than to state the fact of an excess. The removal of the alcohol is considered to be essential, since the specific lævorotatory power of inverted sugar diminishes with progressive increase in the amount of alcohol present; moreover, after removing the alcohol, less lead acetate is required for decolourisation. The evaporation temporarily reduces the rotatory power, but the original rotation is always restored by twenty-four hours' repose after dilution. The presence of alkaline chlorides (derived from the hydrochloric acid used for inversion and the alkali for subsequent neutralisation) increases the rotation, but with the proportions recommended (one-tenth vol. of acid of 1·1 sp. gr.) this is almost exactly compensated for by the evaporation, for in the presence of chlorides the recovery of the rotatory power diminished by evaporation is not complete in twenty-four hours. It is very important to avoid an alkaline reaction at any stage, as even in the cold this soon diminishes the rotation (C. J. Abst. 1890, 426).

For the estimation of sugar by Fehling's solution, the tannin must first be removed by lead acetate, the excess of lead being precipitated by sodium carbonate. Ordinary fully fermented wine usually contains under 0·1 p.c. sugar, and may be decolourised by a small quantity of animal charcoal. After rendering it alkaline with a little caustic alkali or carbonate, 5 c.c. is warmed with 2 c.c. Fehling's solution in a water-bath. If the blue colour completely disappears, the wine contains over 0·2 p.c. sugar. If the blue colour persists, 5 c.c. more wine may be added, and the warming repeated. In this way an approximation to the amount of sugar may be made (C. J. Abst. 1884, 502).

Neubauer has shown that, whilst pure wine which still contains unfermented sugars turns the plane of polarisation to the left, perfectly fermented wine either does not polarise at all, or only a few tenths of degrees of Wild's scale to the right, wines sweetened with so-called potato sugar contain considerable proportions of dextrorotatory non-fermentable substances. The dextrorotatory substances natural to wine are insoluble in strong alcohol, whilst the impurities in potato sugar are mostly soluble. Neubauer recommends that the wine to be tested should be evaporated to one-fifth of the original bulk, and that 90 p.c. alcohol should be added so long as a precipitate is formed. This is separated by filtration, and the filtrate mixed with ether, all optically-active substances being then found in the aqueous fluid separating from the ether.

Nessler and Barth show that it is a matter of considerable importance also to remove the tartaric acid present in the wine, and they add, before precipitating with alcohol, a few drops of a strong potassium acetate solution, thus separating the tartaric acid as acid potassium tartrate.

9. *Detection of added grape sugar* (C. Neubauer, D. P. J. 229, 463). After decolourising, the wine, which, when examined in tubes 220 mm. long with Wild's large polaristrobometer, shows a slight dextrorotation of 0·4 to 0·6° (1° Wild = 4·6043° Soleil = 2·89005° Ventzke-Soleil), 250 to 350 c.c. are concentrated until the salts begin to crystallise out. The concentrated solution is, after the addition of a sufficient quantity of pure animal charcoal, diluted to 50 c.c. and filtered. The filtrate, generally of a faint-yellow colour, shows with most wines a slight dextrorotation in tubes 220 mm. long, which varies with pure Rhine, Haardt, and Mark-Graefler wines, from the years 1874 to 1876, between 0·5 and 2°. The 50 c.c. are next evaporated to a syrupy mass on the water-bath, the residue being treated gradually and with careful stirring with a quantity of 90 p.c. alcohol large enough to throw down all precipitable matter. After having allowed the mixture to stand for six to eight hours, the alcohol is either poured off or filtered off, and the residue extracted with cold water. The solution is decolourised with animal charcoal and filtered. In all natural wine the dextrorotatory substance is chiefly in the alcoholic precipitate. The alcoholic filtrate is evaporated to one-fourth of the volume originally added, and the cold solution treated gradually with four to six times its volume of ether, shaking the mixture the whole time. After standing, a more or less thick aqueous solution separates under the ether, which, in wines containing potato sugar, contains the non-fermentable substances of these preparations, soluble in alcohol (amylin), and consequently shows a strong dextrorotation. After removing the ether the aqueous solution is diluted with water, warmed on the water-bath to expel all ether, decolourised with animal charcoal, and the filtrate diluted, according to the size of the observation tube, to the necessary volume. With pure natural wines of medium growths, which no longer contain unfermented sugar, the dextrorotation of this aqueous solution precipitation from 250 to 350 c.c. of wine is, after discolouration and dilution to 30 c.c., generally either *nil*, or at the most 0·2–0·5°.

All wines having a rotation of 0·1–0·3° to the right may be regarded as perfectly pure. If, however, the dextrorotation is 0·5–0·6°, it is more satisfactory to apply the above-described method (C. J. Abst. 1879, 82).

Tony-Garcin (C. R. 104, 1002) decolourises the wine by means of animal charcoal, and determines its rotatory and reducing power. When the reducing power is equivalent to 2 grms. or less, and the rotatory power is more than +13′, the wine contains some foreign dextro-gyrate substance. If the wine contains more than 2 grms. of reducing matter per litre, 1·5 grm. is deducted, and the remainder is multiplied by 6, and distinguished by the sign +. This is added algebraically to the observed rotatory power expressed in minutes, and if the sum is greater than +13′ the wine probably contains foreign dextro-gyrate substances, and this conclusion is certain if the excess above +13′ is equal to 10′.

The nature of the foreign matter is determined by chemical methods—cane-sugar by inversion; dextrin by saccharification; glucose, in the absence of cane sugar and dextrin, by the relation between the reducing action and rotatory power of the wine.

When polarimeters other than Laurent's are used, it may be taken that the rotatory power of wines free from foreign dextro-gyrate matters is never more than +13′ (C. J. Abst. 1887, 692).

J. Macagno gives the following method of estimating glucose in wine or must (G. 4, 267). Glucose reduces mercuric chloride to the mercurous salt, even at the ordinary temperature. A known amount of a 5 p.c. solution of corrosive sublimate being added to the wine or must, and the unreduced portion being determined with potassium iodide solution, the percentage of glucose will be indicated without introducing the errors which accompany the use of Fehling's reagent. All the sugar of the wine must be turned into glucose, since lævulose and invert sugar require prolonged boiling with the chloride. Neither cane sugar nor any other constituents of the wine, with the exception of the colouring matter, has any action upon mercuric chloride. If the solution be kept concentrated, the error due to the colouring matter disappears (C. J. Abst. 1875, 484).

According to A. Béchamp (C. R. 80, 967), wine, when decolourised, concentrated, and freed from tartrate, sometimes causes polarisation to the right, sometimes to the left, and sometimes has no action. This effect is produced by the presence of two characteristic dextrorotatory substances, one of which (B), although it, like grape sugar, reduces a cupric solution, yet does not ferment in contact with yeast; the other (A) has little or no reducing action (C. R. 54, 1148). The last-mentioned substance—which is neutral, solid, infusible, non-volatile, and tasteless—is soluble in water but insoluble in alcohol. It may be extracted from the wine by carefully evaporating it to one-twelfth of its bulk, and, when the tartrate has crystallised out, throwing it on a filter and washing with alcohol of 40° or 50° (p.c.). On adding twice or thrice its volume of 90 p.c. alcohol to the filtrate, the substance (A) is precipitated. The first-mentioned substance (B) is obtained from the alcoholic filtrate from (A) after removal of the alcohol by distillation and adding to it a solution of barium hydrate in slight excess, so that it is distinctly alkaline. The solution, after the separation of the bulky precipitate, is treated with basic acetate of lead. The precipitate thus obtained is well washed, decomposed by sulphuretted hydrogen, and the solution evaporated at a temperature below 60°. When of the consistence of honey, it is exhausted with alcohol of 95°, dissolved in water, and the barium exactly precipitated by sulphuric acid. The solution is finally evaporated and treated with alcohol as before, when it leaves the new substance, which dries up to a gummy mass without any sign of crystallisation. It has a peculiar acid taste, and strongly reddens litmus. It reduces a cupric solution exactly like glucose.

Besides glucose and these two substances, there are others contained in wine which are also optically active (C. J. Abst. 1875, 748).

According to G. Chancel (C. R. 81, 46), the gummy matters A and B obtained by Béchamp from wine, the former of which is identical with the body described by Pasteur (Etudes sur le Vin, 1866, 213), are too small a quantity to affect seriously the ordinary determination of glucose in wine (C. J. Abst. 1876, 117).

10. *Sulphuric acid* is precipitated directly with barium chloride in wine acidulated with hydrochloric acid, and determined in the ordinary manner.

Wines containing more than 0·92 p.c. sulphuric acid (SO_3), corresponding to 2 grms. potassium sulphate (K_2SO_4), may be regarded as plastered or sulphured. According to Nessler (B. C. 1882, 556), the percentage of sulphuric acid, reckoned as the potassium salt, varies between 0·04 and 0·12. Should the percentage rise to 0·26, the extra amount is probably due to the sulphur employed in the purification of the casks. A normal wine, therefore, contains only 1·3 grm. K_2SO_4 per litre, and the wine ought not to be sold if there be 1·9 grm. present.

11. *Sulphurous acid* is determined by distilling a portion of the wine to which phosphoric acid has been added in a stream of carbonic acid, receiving the distillate in solution of iodine, and determining the sulphuric acid thus formed. The details of the method are as follows (B. Haas, Ber. 15, 154): the wine is distilled in a current of carbon dioxide, and the distillate is collected in a suitable apparatus (a bulbed U-tube) containing 30 to 50 c.c. of iodine solution, containing 5 grms. pure iodine and 7·5 grms. potassium iodine per litre, thus oxidising the sulphurous acid. As soon as the distillate amounts to about half the original volume of the wine used, the contents of the U-tube are washed out, acidulated with hydrochloric acid, precipitated with barium chloride, and the barium sulphate washed, dried, heated to redness, and weighed. This method gives very good results. Wine will absorb as much as 0·36 grm. of sulphurous acid per litre when it is shaken in a barrel in which sulphur has been burnt, and if the treatment is repeated the sulphurous acid will equal 0·5 grm. per litre. Sulphur is burnt in the barrels to prevent the formation of mildew (C. J. Abst. 1882, 773). Opinions vary as to how much sulphurous acid a wine may contain. According to the medical faculty of the University of Vienna, not more than 8 mg. per litre should be allowed, whereas other authorities regard 80 mg. as not an excessive amount.

For the influence of the addition of sulphurous acid solution on the determination of the amount of *potassium sulphate*, *v.* P. Charles (J. Ph. [5] 17, 11; C. J. Abst. 1888, 759).

12. The determination of *phosphoric acid* is to be effected in the ash by the molybdic method. The assumption that the better kinds of wine always contain more phosphoric acid than the poorer ones is unfounded. At the same time the amount of the phosphoric acid can, in many cases, serve as a valuable means of ascertaining the character of a wine, especially of wines used for medical purposes, or of those of a particular district in which the amount of phosphoric acid varies between definite limits.

For remarks on estimation of phosphoric acid in sweet wines, *v.* W. Fresenius, Fr. 28, 67. He finds that in wines containing much sugar a loss of phosphoric acid takes place during the incineration of the residue. A higher result is obtained when the residue is deflagrated with alkaline carbonate and nitrate. Destruction of the sugar by fermentation by addition of very small quantity of yeast leads to the same result.

13. *Cream of tartar* is to be determined by Nessler and Barth's method.

14. A determination of *free tartaric acid* is only required to complete the other analytical results.

To detect free tartaric acid 100 c.c. of wine are evaporated to the consistency of a thin syrup, and mixed with alcohol as long as a precipitate appears. After a few hours all cream of tartar has separated, and to the filtrate $1\frac{1}{2}$ to 2 c.c. of a 20 p.c. solution of calcium acetate are added. Wines free from free tartaric acid remain clear; those with 0·05 p.c. of free tartaric acid give a strong crust of acid tartrate.

For the quantitative determination of free tartaric acid along with that of cream of tartar, the method of B. Haas (Zeit. Nahrungsmittel und Hygiene, 1888, 100) is recommended. Two quantities of 50 c.c. each of the wines are evaporated in dishes on the water-bath to about 4 c.c. One of these is, previously to the concentration, half neutralised with potassium carbonate. After the desired concentration is effected, 2 c.c. of glacial acetic acid is added to each portion, and the hydrogen potassium tartrate is collected and titrated with alkali. The difference between the amounts of hydrogen tartrate as thus determined corresponds with the free tartaric acid in the wine. Borgmann's method consists in evaporating wine to a syrup, precipitating the potassium hydrogen tartrate by alcohol, and filtering, the precipitate being then dissolved in hot water and titrated by soda. The alcoholic filtrate is divided into equal parts, one of which is neutralised with potash and then added to the other. The potassium hydrogen tartrate so produced is then separated as before, and the potassium hydrogen malate should be found in the filtrate. In the presence of much sugar, Gans (Zeit. Ang. Chem. 1889, 669) finds that a portion of the potassium hydrogen tartrate escapes precipitation; while, on the other hand, part of the tartaric acid is retained by the filter, in spite of repeated washings with alcohol. This affects also the tartaric acid estimation, which is further vitiated by a portion of the malic acid not passing into the alcoholic filtrate. In the presence of sugar, however, nearly the whole of the malate is precipitated, and is thereby estimated as tartaric acid, and, at the same time, the amounts of the other errors are altered (C. J. Abst. 1890, 427).

For the estimation of tartaric acid in wine, Berthelot's method, consisting in the separation of the acid in the form of acid potassium tartrate and titration of the latter with normal alkali, is usually employed; but, in addition to other sources of error which have often been pointed out, this method involves the separation of the calcium present in the form of calcium tartrate, which of course is neutral to normal alkali. In a number of determinations of the lime contained in the precipitate, Kayser found the error involved varied from 0·2 to 0·6 p.c. of tartaric acid, and in several instances was larger than the amount of tartaric acid calculated from the acidity only. The error is the greater the older the wine and the smaller the percentage of tartaric acid. The amount of lime has, therefore, to be determined, and an equivalent quantity of tartaric acid to be added to that found acidimetrically by Berthelot's method.

J. Nessler and M. Barth give the following method for estimating free tartaric acid: 50 c.c. of wine are evaporated to a thin syrup; this is well shaken with 70 c.c. of 96 p.c. alcohol, and allowed to stand four hours in a cool place to permit the tartrate to settle out. The precipitate is separated, and its acidity reckoned as tartrate. The filtrate is freed from alcohol, 0·5 c.c. of acidified 20 p.c. solution of potassium acetate is stirred into the syrupy residue, and the newly-formed tartrate is estimated as before. But this method fails in cases of wines strongly plastered, although negative values cannot be obtained, as was sometimes the case with the older methods.

Determination of citric acid. Pure wines are free from citric acid, or contain only slight traces, whilst in falsified wines that acid is not unfrequently met with.

100 c.c. of the wine are evaporated to about 7 c.c. and precipitated with 80 p.c. alcohol. The acidity of the filtrate is partly neutralised by the addition of milk of lime, and the filtrate from the resulting precipitate is diluted to the original bulk of the wine taken. About 1 c.c. of a cold-saturated solution of neutral lead acetate is added, and the precipitate (containing phosphoric, sulphuric, tartaric, citric acids, and part of the malic acid) is collected, decomposed with hydrogen sulphide, and the solution of the free acid rendered alkaline with lime, the calcium phosphate removed by filtration, the filtrate slightly acidified with acetic acid, tartrate of lime separating. From the filtrate calcium citrate separates on prolonged boiling. It is collected and dried at 100°, the precipitate corresponding to the formula $(C_2H_5O_7)_2Ca_3+4H_2O$ (C. J. Abst. 1882, 999).

Schmidt and Hiepe (Fr. 21, 534) operate as follows: 200 c.c. of wine is evaporated to about one-half, and basic lead acetate is added until the reaction is alkaline. The precipitate is washed with cold water, decomposed with H_2S, and the solution of the acids thus obtained is concentrated until about 50 c.c. are left; this is exactly neutralised with potash and further concentrated. An excess of a saturated calcium acetate solution is added, and after 4–6 hours the precipitate is separated, washed until the fluid amounts to 100 c.c., ignited, and the alkalinity determined by standard hydrochloric acid. From the volume of normal acid used the amount of tartaric acid is calculated, and 0·286 grm. is added as a correction for the solubility of the calcium tartrate.

The filtrate from the calcium precipitate is again concentrated to 20–30 c.c. and 60–90 c.c. of 96 p.c. alcohol is added. The precipitate of calcium malate, succinate (tartrate), and sulphate is collected, dried at 100°, and weighed. It is then dissolved in the minimum quantity of hot dilute HCl, the solution rendered slightly alkaline with potassium carbonate, and the precipitated calcium carbonate separated by filtration. After neutralisation with acetic acid, the filtrate is concentrated to a very small bulk and then precipitated hot with barium chloride, the precipitate consisting of barium sulphate and succinate. From it the barium succinate is extracted with dilute hydrochloric acid, the barium estimated as sulphate, and from the weight of the latter the amount of succinic acid is calculated : $233BaSO_4 = 118C_4H_6O_4$. The weights of the sulphuric, succinic, and tartaric acids (0·0286 grm. tartaric acid) are then calculated into the corresponding calcium malate, 172 parts of which correspond to 134 of malic acid (C. J. Abst. 1883, 384).

In natural wines containing free acids up to 8 grms. per litre the amount of the free tartaric acid is not more than a sixth, or, at most, a fifth, of the 'non-volatile acids.' In natural wines, containing a higher amount of free acid, the quantity of the free tartaric acid is frequently much larger.

15. *Examination for colouring matters.* (*a*) *Vegetable colours.* The wine is mixed with an excess of lead acetate and filtered. The colour of the precipitate in a genuine red wine may be greyish-blue, bluish-grey, ash colour, or greenish. If a precipitate is obtained not greatly differing from these colours, the search for other vegetable pigments can give no certain result. The colouring matter of bilberries gives a blue precipitate ; mallow and elderberries a green. The colour of Phytolacca berries differs from that of red wine by giving a red-violet lead precipitate.

(*b*) *Tar colours.* As the colouring of any article of food, &c., with tar colours is illegal, it is in general sufficient to prove the presence of any such colouring matter in wine. In most cases the presence of a tar colour may be recognised in wine by the following methods :

a. By shaking the filtrate from the basic lead acetate with amyl alcohol, and testing the coloured amyl alcohol. For this purpose we require 100 c.c. of wine and 30 c.c. of solution of basic lead acetate.

b. By the wool test, according to Strohmer and Arata (dyeing wool).

c. By Cazeneuve's oxide test (Vierteljahrschrift für Chemie der Nahrungsmittel, 1886, 80 ; C. R. 102, 52).

The oxides employed are yellow mercuric oxide in the proportion of 0·2 grm. per 10 c.c. of wine ; lead hydroxide, containing 50 p.c. of water, in the proportion of 2 grms. per 10 c.c. ; and gelatinous ferric hydroxide, containing 90 p.c. of water, in the proportion of 10 grms. per 10 c.c.

Mercuric oxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, erythrosin, eosin J, methylene blue, Coupier's blue, and diphenylamine blue. It partially absorbs orange I., saffranine, chrysoidine, chrysoine, methyleosin, yellow II., red NN, red I., and Ponceau RR. It does not absorb the sulpho-conjugated derivative of rosaniline, Bordeaux red B, Ponceau R, Ponceau B, orange R, orange RRR, orange II., orange RR, tropæoline M, tropæoline II., yellow I., solid yellow, dinitronaphthol yellow, U. S. yellow.

Lead hydroxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, methylene blue, Coupier's blue, diphenylamine blue, and erythrosin. It differs from mercuric oxide in not absorbing the rosanilines, and also in absorbing the sulpho-conjugated derivative of rosaniline, Bordeaux red B, the purple red, and soluble red of rocelline.

Ferric hydroxide does not absorb erythrosin, the sulpho-conjugated derivative of rosaniline, Bordeaux red B, purple red, soluble red, and solid yellow. It absorbs the natural colouring matter and foreign vegetable colours, cochineal, and all the derivatives of rosaniline, except the sulpho-conjugated derivative.

Zinc hydroxides and stannous hydroxide behave similarly. The latter retains the natural colouring matter, but does not absorb cochineal or orchil. After the wine has been treated with the hydroxides, the colouring matters must be distinguished by special tests. If the wine is treated with magnesia and hot amyl alcohol, a number of blues which are precipitated by the above-mentioned hydroxides can be isolated and distinguished.

C. Blarez and G. Denigés distinguish the natural colouring matters of wine from added coal-tar colours (B. 46, 148) as follows : 10 c.c. of the wine is treated with 10 drops of glacial acetic acid, heated to 100°, and 0·2 grm. of powdered mercuric acid added, the mixture shaken rapidly, cooled, and filtered ; any coal-tar colouring matters then pass through into the filtrate, whilst all the natural wine colouring matters remain in the filter as a lake. When only a mere trace of the artificial colouring matter is present, it may not be readily seen in the filtrate, and may be partly held by the precipitate. In this case the precipitate is drained, and then washed by pouring 5 or 6 c.c. of alcohol containing some drops of acetic acid through the filter several times, by which means any coal-tar colours are extracted.

Genuine red wine treated with caustic lime becomes brown, or dirty bluish-grey gradually changing to brown. Occasionally a greenish colour appears momentarily. Whortleberry juice or caustic lime becomes deep blue, then gradually green ; madder instantly becomes green ; the juice of Phytolacca berries becomes yellow, and fuchsine becomes colourless. A piece of chalk moistened with the wine, if genuine, becomes brown or slate-grey ; if the wine is coloured the stain becomes, in presence of whortleberry, blue or violet ; with mallow, blue or green ; with Phytolacca berries and fuchsine, no change ; *v.* table on next page.

New red wine is quickly decolourised by nascent hydrogen ; old wine very slowly (C. J. Abst. 1877, 938).

The following two tests are recommended in addition :—

d. Shaking the wine with ether before and after supersaturation with ammonia.

Five to 6 c.c. of the wine to be tested are poured into a glass test-tube of about 20 c.c. capacity, and then three-quarters of its bulk of ether is added. After a few minutes the ether rises to the surface of the coloured or not coloured wine. If the ether be coloured yellow, and assumes, on addition of some drops of ammonia, a deep-red tint, Campeachy-wood has been used to colour the wine. If the ether become red and violet, and remains so even on addition of a large quantity of ammonia, the wine contains colouring matter derived from some of the lichens.

If the red-coloured ether lose its tint on mixing with ammonia, without passing into violet, then only the natural colouring matter of the wine, œnolin, is present. If the red-

—	Hydrogen (Zn and HCl)	$(NH_4)HO$	KHO conc.	$CuSO_4$	Amyl alcohol
Mallow . .	Decolourised after short time	Green, passing to yellow	Brown	Intense blue	Dissolves much colouring matter on shaking with red colour
Kermesberry (Phytolacca)	Decolourised after 12 hrs.	Yellow	Yellow	Dark brown, becoming green	No trace of colouring matter dissolved
Whortleberry juice	Decolourised very slowly 12 to 24 hrs.	First violet, passing to red, and lastly to brown		Splendid violet	Takes up almost all colouring matter with intense colour
Fuchsine .	Decolourised instantly	Decolourised		—	Ditto
Genuine wine	Decolourised after a time	Becomes gradually brown	As with $(NH_4)HO$	Slowly becomes brown	Takes up a little colouring matter, becoming red

Hilger (D. P. J. 125, 310).

coloured ether loses its red tint with ammonia, without imparting any colour to the latter, then fuchsine has been added to the wine. When the ether rises uncoloured, a fresh sample of the wine to be tested is taken, twice its volume of water is poured into it, and half its volume of ammonia added. If the wine now assumes a brownish-red colour, it contains cochineal; on the contrary, if it turns green, then it can be assumed that none of the substances mentioned are present (Mellias, D. P. J. 215, 383; C. J. Abst. 1876, 117).

A substance, known as *Tintura por los vinos*, is largely used in the district of Huesca for colouring Spanish wines. It contains two coal-tar derivatives, one of which is that form of Biebrich red which is turned blue by sulphuric acid, whilst the other, which exists in smaller proportion, closely resembles the colouring matter known as *cérise*. The composition of the *tintura* is:

Organic matter, mainly Biebrich red, 66·4 sodium sulphate; anhydrous, 26·10; arsenious oxide, 1·62; loss, iron, lime, &c., 5·88 = 100. The presence of arsenic is of special importance (Jay, Bl. 42, 167; C. J. Abst. 1885, 309).

In testing for coal-tar colours in wines by adding ammonia to alkaline reaction and shaking with amyl alcohol, it is necessary to avoid a great excess of ammonia, and the proportion of the latter should never be more than 3 p.c., for if this is exceeded the amyl alcohol may remain colourless, even if the wine contains a coal-tar colour. If the amyl alcohol is colourless it should be decanted off, filtered, and evaporated with a small quantity of silk, when the foreign colouring matter, if present, will become fixed on the silk (Jay, *l.c.*).

To detect oxyazo- colouring matters, a sample of the liquid or an alcoholic extract of the solid is evaporated to one-half, so that nearly all the alcohol is dispersed. Pure wool is then boiled for ten to twenty minutes in the liquid. The results will be as follows:—Ponceau R, dark red; Ponceau RR, light red; Bordeaux B, bluish; Bordeaux red, Bordeaux R, reddish; Bordeaux red, crocein scarlet, violet red, Biebrich scarlet, violet red. If the dyed wool is dried and then moistened with concentrated sulphuric acid, the first two will be fiery red, the next three deep indigo-blue, whilst the last will assume a dark-green colour. Pure red wine dyes wool a dirty brownish-red, which under the influence of the acid is changed to a dirty brown (F. Strohmer, B. C. 1885, 648; C. J. Abst. 1886, 183).

The formation of isonitriles when aniline derivatives are warmed with potash and chloroform serves for the direct determination in wine of even minute traces of many of the aniline colours. The evolution of the isonitrile is accelerated by adding excess of strong sulphuric acid (Curtman, Fr. 26, 555; C. J. Abst. 1887, 1147).

J. Herz (Chem. Zeit. 10, 968) gives the following process. 30–50 c.c. of the wine—or, if the quantity of colouring matter in the wine is small, 100 c.c.—is concentrated to 30 c.c.; 20–30 c.c. of a saturated solution of magnesium sulphate, and 10–20 c.c. of soda solution are added, stirring well. If necessary, the treatment is repeated until the liquid is colourless or nearly so. The filtrate is made acid with dilute sulphuric acid (1·3), and if sulphonic acid colours are present the red colour reappears. The most commonly-used member of this group, acid-magenta (rosaniline-sulphonic acid), yields a violet-red solution, and can be estimated by comparing the tint with magenta solutions of known strength. One mg. of magenta per litre can be distinctly detected in 30 c.c. of wine without previous concentration. When archil (orseille) colours are present, the filtrate is bluish, and when made acid turns a litmus-red colour. To test for magenta under such circumstances, Blarez's method of shaking with lead dioxide is used; this destroys the orseille and natural colour. Cazeneuve's method is not recommended. To test for other colours in the magnesium hydroxide precipitate, the gelatinous mass is stirred up with hot water, allowed to settle, and the liquid decanted off. If only the natural colour of the wine is present, or *bilberry* has been used, this liquid is yellow-brown; if *archil* has been used, dark violet; if *Ponceau*, onion or *Ponceau* red; if *cassissine*, pale red or dark yellow; if *vinicoline bordelaise*, a yellow-red or a yellow-brown liquid, which, when poured on sulphuric acid, gives a violet ring. By shaking the coloured liquid with amyl alcohol, *Ponceau* yields an onion-red residue; *vinicoline*, a dark-brown one; *cassissine*, a dirty green, violet at the edge, turned yellow by strong hydrochloric acid. The precipitate is a dark-grey or brownish-grey colour when the natural or vegetable colours only are present; with *archil* it is violet; with *magenta* (acid or ordinary), dirty white; with *cassissine*, dirty yellow-brown; with *vinicoline*, crimson-red. The precipitate is mixed with sand, dried, and extracted with ether; the extract contains any ordinary magenta, which can be identified in the usual manner by dyeing wool, or *cassissine* which dyes wool red-brown, and leaves a yellow-brown residue in the dish. The dyed wool becomes yellow when treated with strong hydrochloric acid, and colourless with ammonia. When wine is shaken with amyl alcohol and the coloured extract evaporated, the residue, if it contains the substances named, behaves in the manner described below:

—	—	With concentrated		
		H_2SO_4	HCl	NaHO
Archil	Violet-red	Blue	Red	Blue
Bordeaux B.	Carmine	Carmine	Carmine	Carmine
Ponceau R.R.R.	Dark-red	Crimson	Crimson	Brown
Cassissine	Violet-purple	Yellow	Yellow-brown	Red
Vinicoline-bordelaise	Cherry-red	Brown	Red	Brown

whilst the wine after extraction is cherry-red with ordinary *magenta*, violet-red with *acid magenta*, dark cherry with *Bordeaux*, yellow-red with *Ponceau*. Wine coloured with *magenta* produces a violet froth. The detection of vegetable colouring matters in presence of the natural colour of wine or otherwise is a matter of great difficulty, and most of the known methods are ineffectual. It is, however, effected by Herz with comparative facility in the following manner: 10 to 15 c.c. of wine is shaken with 5 c.c. of a saturated solution of tartar emetic, and then examined by reflected and transmitted light either at once, or, if no immediate change has taken place, after some time. This treatment produces with genuine red wine always a cherry-red colour, and with other substances as follows:

Red poppy (*Papaver Rhœas*), dark cherry-red; violet commercial *elder* colouring matter, red-violet; *bilberry* (*Vaccinium myrtillus*), blue-violet; *privet-berry*, pure violet. White wines artificially coloured, and red wines mixed with artificial colours have been successfully examined in this manner; in the latter case the wine, some time after treatment, is compared with a genuine red wine to distinguish more readily the change of colour. Old solutions of privet do not give the colour change. Sodium hydrogen carbonate produces with pure wine brown-red; with wine coloured with pure *elderberry* grey-violet, and with *bilberry* brown-green. Tartar emetic appears to form an antimony lake with the colouring matters. With practice, all the above-mentioned colours can be detected in 30–50 c.c. of wine (C. J. Abst. 1887, 92). According to A. Dupré (An. 1, 193), fraudulent colouring matters added to red wines may be detected by dialysis, which is best accomplished by placing in the wine a cube of jelly about $\frac{3}{4}$-inch square. These cubes are made by dissolving 5 grms. of gelatine in 100 c.c. of warm water, and pouring the solution into flat paper moulds; from the plate thus obtained the cubes are cut. After twenty-four to forty-eight hours the cube, on examination by transmitted light, will be found to be coloured more or less deeply by any colouring matter present, excepting the natural colouring matter, which penetrates only to a depth of $\frac{1}{8}$-inch at the most. The nature of the colouring matter may be determined either by the colour of the jelly, or spectroscopically, or by the action of dilute ammonia. The colouring matters which penetrate jelly but slowly are those of pure wine and of rhatany-root; whereas rosaniline, cochineal, logwood, brazilwood, indigo, litmus, red cabbage, beet-root, *Malva sylvestris*, and *Althea officinalis* penetrate rapidly into jelly (C. J. Abst. 1877, 227); *v.* SPECTRUM ANALYSIS.

Girard and Gautier employ tablets of plaster of Paris (Spica suggests tablets of *magnesia alba* instead) immersed in egg albumen and dried. A drop of the wine to be examined is let fall on such a prepared tablet, and the colour of the stain produced is observed. The natural colouring matters of wine give a yellowish-brown; those containing rosaniline or 'vinoline' (apparently a crude fuchsine paste), a reddish yellow; those with indigo, an azure-green; with archil, a violet-red; and those with amaranth, a greyish-violet stain. Another method consists in shaking up the wine with baryta, water, and amyl alcohol, when the latter extracts the colouring matter.

Soutegné (C. C. 1889, 550) treats the wine with $\frac{1}{10}$ volume of 10 p.c. potash, stirs for five minutes, and pours the liquid into a parchment-plaited filter standing in water. After a few hours the yellow oxidation products of the tannin begin to pass. At the end of twenty-four to forty-eight hours the foreign colouring matters have become fixed on the parchment, which may be judged by their colour. Natural wine simply colours the parchment yellow.

Alkanna-red is very easily taken up from its solutions by amyl alcohol. On adding to the amyl alcohol solution a few drops of olive oil or oil of almonds and evaporating off the alcohol, the oily residue (after washing with water) has a fine red colour, which on saponification becomes a rich blue, or, if the alkanna used was old, a green (Herz, Fr. 23, 637; C. J. Abst. 1890, 311).

For purposes of wine adulteration the following substances are generally used: Fuchsine and the various preparations termed caramels, ammoniacal cochineal, sulphindigotic acid, logwood, and the lichen reds.

All these bodies are precipitated by basic acetate of lead; fuchsine, however, if present in considerable quantity, is only partially precipitated. The remainder, which colours the filtrate rose, may be separated by agitation with amyl alcohol.

The lead precipitate is treated with a dilute solution of potassium carbonate (2 grms. to 100 of water); the cochineal and sulphindigotic acid are thus dissolved out, together with the fuchsine contained in the precipitate. From this liquor the fuchsine is separated by neutralisation with acetic acid and agitation with amyl alcohol. The rose-coloured liquid thus obtained is identified as a solution of fuchsine by means of the spectroscope.

The solution, now containing the potassic salts of carminamic and sulphindigotic acid, is treated with a drop of sulphuric acid and again shaken with amyl alcohol. The carminamic acid is now dissolved out, and may easily be identified by means of the spectroscope; three dark bands are seen, one between the lines D and E, the second in the green, and the third, less marked, in the blue.

The indigo now left in the solution is detected by the blue colour and the absorption-band seen between C and D.

That part of the original lead precipitate which was insoluble in potassium carbonate is now treated with a 2 p.c. solution of potassium sulphide, which dissolves the colouring matters of the logwood and of the wine itself. The logwood colouring matter may be thus extracted, but it is simpler to test for it directly in the wine by addition of calcium carbonate and two or three drops of lime-water. The filtered liquid is almost colourless in the case of a natural wine, but is of a fine red colour if logwood is present.

The lichen red is detected by washing the insoluble portion left after treatment with potassium sulphide and dissolving it in alcohol; a red colour and a definite absorption-band then reveal its presence (G. Chancel, C. R. 84, 348; C. J. Abst. 1877, 371).

Palmieri and Casovia (C. C. 1888, 1594) dip a strip of flannel into the wine previously heated to 70–80° and to which aluminium acetate has been added. Pure wine colours it yellowish-brown; if archil is present it is coloured amaranth-red. A still better test is to render the wine alkaline with barium hydroxide, and to boil the flannel in the filtrate. Pure wines do not colour it, but archil dyes it amaranth-red, which becomes violet when treated with ammonia. The ether extract of natural wine becomes decolourised by ammonia, whereas in the presence of archil it is coloured violet.

Flannel dipped in hot dark-coloured wines and afterwards treated with ammonia becomes greenish if pure; cochineal causes a fast red, archil a violet, and magenta a fugitive red colour (C. J. Abst. 1889, 655).

The fresh colouring matters of *bilberries* and wines are similar but not identical, and, according to H. W. Vogel (Ber. 21, 1746), they are readily distinguished by their absorption spectra after careful neutralisation with ammonia, or, better still, when they are treated with a trace of alum before addition of ammonia. Care must be taken that the wine is not too concentrated or the ammonia in too great excess.

Detection of logwood in wine. A. Pizzi (G. 11, 120). When a solution of logwood is treated with manganese dioxide it becomes brown, and this brown liquid, by the action of zinc and hydrochloric acid, gives a colourless solution of hæmatoxylin. This may be detected by the ordinary reagents for that substance, alkalis and their carbonates giving a blue-violet colouration, calcium hydroxide a red-violet, tin dichloride or ammonium molybdate, in a solution slightly acid with nitric acid, a violet colouration. Advantage has been taken of this reaction for the detection of logwood in wines. 20 c.c. of the wine is agitated with 2 grms. finely powdered manganese dioxide, filtered, and the brown liquid treated with zinc and hydrochloric acid, which reduces the oxidised logwood colouring matter to hæmatoxylin. The solution is then divided into several portions, and tested with the reagents given above. Pizzi has examined wines to which other red colouring matters have been added, and although these yield brown solutions with manganese dioxide the reduced solution does not give the hæmatoxylin reactions. Brazilwood is the only one which has any analogy with logwood, but here also there are differences (C. J. Abst. 1881, 761).

Beetroot juice is used in colouring wines for the purpose of concealing the presence of magenta. The absorption-bands of magenta are hidden by those of beetroot, but if a few drops of copper sulphate solution are added to the wine, the beetroot bands gradually vanish and the magenta spectrum becomes visible.

To detect magenta in presence of an extract of the flowers of the wild poppy, *Papaver Rhœas*, 1 drop of iodine solution (0·1 grm. per c.c.) is added to the wine before examination with the spectroscope (F. v. Lepel, B. 11, 1552; C. J. Abst. 1879, 82).

Special tests for the detection of fuchsine in wine. Fuchsine or rosaniline used to colour wines may be detected by the following methods (E. Jacquemin, C. R. 83, 70):

1. A small quantity of gun-cotton is heated for a few minutes in 10–20 c.c. of the wine to be tested, and then washed with water. The colour thereby communicated to the gun-cotton by rosaniline if present resembles that of archil, which is also used to colour wines. The two colouring matters may, however, be readily distinguished by means of ammonia, which turns archil violet but decolourises rosaniline.

2. The wine (100 c.c.) is first heated till alcohol is nearly expelled, a thread of white embroidery wool, previously wetted, is then immersed in it, and the liquid is slowly boiled down to half its bulk. If fuchsine is present, the wool retains, after washing, the colour of that substance. Archil dyes wool a similar colour, but the two colouring matters are readily distinguished by the behaviour of the dyed wool with ammonia.

3. A quantity of the wine (100-200 c.c.) is heated in an open vessel till alcohol is almost completely driven off, then allowed to cool, mixed with excess of ammonia, and finally shaken with ether, which dissolves ammoniacal fuchsine if present. On evaporating the ethereal solution, white wool immersed in it acquires the characteristic colour of fuchsine (C. J. Abst. 1876, 667).

According to L. Lamattina (C. R. 83, 564), fuchsine may be detected by mixing 100 grms. of the wine with 15 grms. of coarsely-powdered manganese dioxide, shaking for twelve or fifteen minutes, and filtering through a double filter paper. If the wine is pure, it passes through colourless; if adulterated, some artificial colouring matter has been used. If pure peroxide is used this process is unexceptionable, but if the manganese contains iron the acid of the wine dissolves it, and it forms an insoluble lake with the colours which remain on the filter. If in this case the residue on the filter is treated with alcohol, the fuchsine dissolves, and may be immediately recognised by adding strong acid and a few drops of ammonia (C. J. Abst. 1876, 668).

G. M. Fordos (C. R. 83, 980) directs that 10 c.c. of the wine should be shaken with 1 c.c. of pure ammonia; 5 to 10 c.c. of chloroform are then added, the test tube several times inverted but not shaken, and the chloroform, after separation by a tap-funnel, heated in a porcelain dish with a piece of white silk immersed in it. When the chloroform is nearly evaporated a little water is added, and the heating continued; all the fuchsine is thus fixed on the silk, which becomes more or less rose-coloured if fuchsine is present. A little water is added to it, and then it is saturated with acetic acid. The fuchsine now separates from the chloroform, and its aqueous solution floats on that liquid. Another modification is to use only 5 c.c. of chloroform, and when this has settled to the bottom of the tube to drop in a crystal of citric acid. The ammonia being saturated, the fuchsine appears on the crystal (C. J. Abst. 1877, 750).

This method permits of the detection of extremely small quantities of fuchsine, especially if the wine be concentrated and a very small piece of silk be used. Quantitative results might be obtained by means of a series of pieces of silk coloured more or less deeply, with which the piece coloured by the wine under examination might be compared.

F. König (B. 13, 2263) boils about half-a-gram of white woollen thread in 50 c.c. of the wine, to which sufficient ammonia has been added to change its colour to a dirty green. After the excess of ammonia has been expelled by boiling, the wool is washed with water, and pressed and moistened with a solution of potash. On heating the wool in a test-tube it dissolves, forming a brown liquid, which is mixed with half its volume of pure alcohol and extracted with ether. On the addition of a few drops of acetic acid to the ethereal solution, a red colouration will be produced if the wine contains even a trace of rosaniline (C. J. Abst. 1881, 314).

Detection of rosaniline hydrochloride by means of stearin. The wine to be tested is warmed, and then shaken with a piece of stearin, which becomes dyed the characteristic colour if rosaniline hydrochloride be present; natural wine only discolours the stearin. Sodium rosaniline sulphonate—which is more frequently used than the rosaniline hydrochloride for colouring wines, both because the colour is more stable and more like wine colour—only dyes stearin blue-violet; in neutral solutions this reaction is not very sensitive. The presence of the rosaniline hydrochloride on the stearin may be rendered evident by treating it with amyl alcohol, which on warming becomes coloured red, and by spectroscopic examination shows the rosaniline absorption spectrum, even when only a trace of the dye-matter is present (Wolff, C. C. [3] 13, 670; C. J. Abst. 1883, 384).

For the quantitative estimation of *magenta* in wine the following modification of Falière's method is recommended by Nessler and Barth (Fr. 1884, 318):

100 c.c. of the wine are mixed with 5 c.c. strong ammonia, and well shaken with 30 c.c. ether. 20 c.c. of the ether are drawn off, and evaporated in a little basin containing a thread of white wool 5 cm. long. Other threads are then dyed with known quantities of magenta, and from the comparison of tints the amount of the added colouring matter in the wine is inferred. The standard woollen threads, inclosed in sealed glass tubes and kept in the dark, do not alter in tint by keeping.

Thomas (Ar. Ph. [3] 21, 304) detects *Bordeaux red* by absorbing the colouring matter from the wine by silk, which is washed with cold water and then heated with boiling water, when the artificial colouring matter is dissolved but the natural colouring matter remains on the silk. In the red liquid so obtained, sulphuric acid develops a violet colour and ammonia a chestnut-brown. In the estimation of the potassium sulphate by precipitation as barium sulphate the Bordeaux red is carried down with the precipitate, to which it remains attached. When this precipitate is ignited, an aromatic odour resembling naphthalene and nitrobenzene is noticed.

Magenta is not decolourised by manganese peroxide; but the juice of bilberries, elderberries, red and blue woods, cochineal, and archil are all altered in colour. Cochineal is decolourised; but the red in wines is changed to brown-yellow.

16. *Salicylic acid* is best sought for by shaking the wine with carbon disulphide or a mixture of equal volumes of ether and petroleum ether, evaporating down, and testing the residue with ferric chloride. If much more than 100 c.c. of wine are used, a faint colour may be occasioned by the normal constituents of wine.

Röse (C. C. 1886, 412) gives the following details of the method. The wine is acidified with sulphuric acid and shaken with its own volume of a mixture of equal parts of ether and light petroleum. The ethereal layer is filtered and distilled down to a few cubic centimetres. The residue is mixed, whilst hot, with a little water, then with a few drops of weak ferric chloride, and is filtered through a wet filter. If salicylic acid is present, the filtrate is violet-coloured; 0·1 mg. per litre can be detected. Should the addition of ferric chloride produce a tannic acid reaction, it is necessary to re-acidify, dilute, and again extract with the ether mixture. The second residue will give the reaction of salicylic acid, of which 0·2 mg. per litre can be detected even in wines containing much tannic acid (C. J. Abst. 1886, 924).

Medicus (C. C. 1890, 2, 28) recommends that 10 c.c. of wine shall be extracted for salicylic acid, instead of 100 c.c., as suggested by Röse, and that the residue of the extract shall be treated with at least 10 c.c. of water instead of 5 c.c. (C. J. Abst. 1890, 1475).

The ferric chloride solution cannot be added directly to strongly-coloured wines and fruit juices, as a coloured precipitate is formed. Previous decolourisation by means of animal charcoal also removes the greater part of the salicylic acid. Weigert (Fr. 1880, 45) adds 5 c.c. of amyl alcohol to 50 c.c. of wine, and shakes well together for some minutes. After standing, the upper layer of amyl alcohol is removed and treated with an equal quantity of alcohol. To this solution some drops of dilute ferric chloride solution are added, when the characteristic deep violet colouration, if salicylic acid is present, is produced.

For the rapid estimation of salicylic acid in wines &c., A. Remont (C. R. 95, 786) prepares a solution of salicylic acid to serve as a standard of comparison. 50 c.c. of a liquid analogous to that to be tested are taken, and into it is introduced the maximum amount of salicylic acid allowed by law. This is then shaken several times with 50 c.c. of ether, and the whole left at rest for a time. 25 c.c. of the ethereal solution are then taken and evaporated at a temperature below its boiling-point in the presence of 10 c.c. of water, so that the latter dissolves the salicylic acid from the ether as it volatilises. The 10 c.c. of water are then made up to 25 c.c., and the liquid thus prepared is used as a standard of comparison.

In testing a wine, 10 c.c. are treated with 10 c.c. of ether. 5 c.c. of the ethereal solution are then evaporated, as described above, with 1 c.c. of water, which is then made up to 5 c.c. This is placed, with the wash-water, in a glass vessel of 30 c.c. capacity and of 15 mm. internal diameter, the standard liquid being placed in an exactly similar vessel. A solution of ferric chloride containing 10 grms. to the litre is then added drop by drop to both vessels until the colour no longer deepens (three or four drops usually suffice). The comparison of the depth of tint is sufficient to decide whether the liquid tested contains more or less salicylic acid than the standard.

It is always advisable to take as a standard of comparison a liquid similar to that to be tested. The method is applicable, without modification, to fruits and syrups (C. J. Abst. 1883, 245).

17. For detecting *saccharine*, C. Schmitt's method is recommended. The wine is shaken up with a mixture of equal parts of ether and petroleum ether, and the evaporated residue melted with sodium hydrate and tested for salicylic acid. Not more than 100 c.c. of wine should be used for this test.

18. *Nitric acid* is sought for by adding 1 to 3 drops of wine to a solution of diphenylamine in (pure) concentrated sulphuric acid.

To detect *sulphurous acid*, *salicylic acid*, and *metals* in wine and must, Ulbricht (C. C. 1884, 684) proceeds as follows: 100 c.c. wine, or 50 c.c. must, and 50 c.c. water are distilled, and the distillate is collected in a receiver containing 5 c.c. of a solution of which 1 litre contains 5 grms. iodine and 7·5 grms. potassium iodide. After 10 c.c. are distilled over, the contents of the receiver are tested with some drops of hydrochloric acid and barium chloride. Without interrupting the distillation, the next fraction is collected in a receiver containing a drop of ferric chloride. If the sample contains only 0·03 grm. salicylic acid per litre, the well-known reaction immediately appears. The distillation is continued until 50 c.c. has passed into the second receiver. The residue can be tested for metals by hydrogen sulphide &c. (C. J. Abst. 1885, 692).

Detection of copper. 200 c.c. of wine is concentrated to one-fifth, and strongly acidified with hydrochloric acid, when a small zinc-platinum couple is immersed. Any copper which may be present is deposited on the platinum plate within twenty-four hours (Gigli, Ar. Ph. [3] 26, 273; C. J. Abst. 1888, 873).

According to Baumert (B. 21, 3,290), *boric acid* is present in many wines, as well as in the leaves and tendrils of the grape-vine (*cf.* Ripper Weinbau u. Weinhandel, No. 36, 1888, and Solstein, Ph. Zeit. 33, 312).

19. *Examination of plastered wine* (M. Bretel, J. Ph. [4] 22, 187). It was shown by Bussy and Buignet that plastered wines contain potash in the form of bitartrate and bisulphate in equivalent proportions. Such a mixture should furnish neutral sulphate on calcination, and the complete absence of carbonates in the ash of plastered wines has been further proved by analysis. Even when plastered to so small an extent as 250 grms. per hectolitre (one-eighth the usual quantity) the ash gave no effervescence with hydrochloric acid. Sulphuretted hydrogen, it is true, was evolved in small quantities, but without effervescence. 250 grms. of the wine are evaporated on a sand-bath, and when the residue becomes syrupy the desiccation is continued in a platinum crucible, heated gently at first, and then incinerated. While still warm the ashes are treated with dilute hydrochloric acid, which in a natural wine always causes brisk effervescence of carbonic acid, but in a plastered wine only a little sulphuretted hydrogen is evolved. This simple method has the further advantage of leaving in hand the solution of the ash, from which useful confirmatory evidence can be obtained.

Suppose alum had been added to the wine, an ash would be obtained free from carbonates, and, according to the above test, plastered. But only a large quantity of alum could have this effect. Experiment showed that up to 200 grms. per hectolitre there was always manifest evolution of gas, and above that quantity the tests would leave no doubt as to the nature of the adulteration (Bretel, J. Ph. [4] 22, 187; C. J. Abst. 1876, 117).

Determination of alum and gypsum in wine (Louvet, C. C. 188, 252). 200 c.c. of wine are evaporated to dryness, the residue incinerated, and the ash fused in a platinum crucible with 3 grms. sodium carbonate, whereby the lime, magnesia, and ferric oxide are converted into insoluble carbonates. The mass is dissolved in water, and the solution filtered. As the solution may contain sodium aluminate, it is acidified with hydrochloric acid treated with a large excess of sodium carbonate, and the alumina collected on a tared filter. The filtrate contains all the alkaline bases. The insoluble portion of the fused mass, containing the chief portion of the alumina, is fused with a few grms. of pure soda, and the fused product digested several times with water. The solutions are mixed together, and treated for aluminium as above mentioned. The precipitate is collected off the tared filter previously used, after being washed several times with distilled water by decantation. It is then dried, ignited, and weighed. In order to determine gypsum in wine, Marty ignites the evaporated residue and treats the ash with very dilute nitric acid. The mixture is then filtered, precipitated with barium chloride, and weighed as barium sulphate (C. J. Abst. 1882, 96).

To determine the extent of 'plastering' which the wine has undergone, and which is permitted only to the extent that not more than 2 grms. potassium sulphate shall be contained in the litre, 5·9695 grms. barium chloride are dissolved in 900 c.c. of water, and, 20 c.c. concentrated hydrochloric acid having been added, the whole is made up to a litre. 20 c.c. of this solution are equivalent to 2 grms. K_2SO_4 per litre when 20 c.c. of the wine are employed. If, on the addition of 20 c.c. barium solution to 50 c.c. of wine, the whole of the sulphate is not precipitated, then the wine is to be rejected (Jay, B. C. 1881, 574; C. J. Abst. 1882, 96).

E. Houdard (Bl. [2] 36, 546) has devised the following method. The apparatus required consists of ten test-tubes, in two rows of five each, a 25 c.c. pipette graduated in 5 c.c., and a burette graduated in five divisions in such a way that each division is 0·5 c.c. larger than the preceding one. 5 c.c. of the wine to be tested are run from the pipette into each of the first row of test tubes, and Marty's standard solution (10 c.c. = 0·1 grm. potassium sulphate) is then added in such a way that a quantity corresponding to the first division (0·5 c.c.) is added to the first tube, a quantity corresponding to the second division (1·0 c.c.) to the second tube, and so on. Boil; filter the contents of each tube into the corresponding tube of the second row, and then add a drop of the standard solution to each tube, and observe in which a slight turbidity is produced. If a turbidity is produced, for example, in tube No. 2, but not in No. 3, then the wine contains more than 2 grms. potassium sulphate per litre but less than 3 grms. With practice, the amount of sulphate may be rapidly estimated to within 0·25 grm. per litre (C. J. Abst. 1882, 425).

Quantities and value of the imports of wine into this country during the year ending December 31, 1891.

Country	Quantity	Value
	Gallons	£
France . . .	6,118,398	3,253,491
Portugal . . .	4,326,121	1,275,678
Spain . .	4,067,761	862,051
Germany . .	567,129	71,664
Italy .	528,665	100,123
Holland . . .	424,725	254,095
Australasia .	381,731	71,361
Madeira . . .	81,700	31,412
British South Africa	12,935	4,224
Other countries .	272,873	71,034
Total . .	16,782,038	5,995,133

WINE GUM *v.* Gums.

WOAD (Fr. *Vouède, Pastel*; Ger. *Waid*).

This commercial product is a dark clay-like preparation made from the leaves of the woad-plant, *Isatis tinctoria*, an erect, herbaceous, biennial plant, belonging to the *Cruciferæ*, bearing yellow flowers, small flat elliptical pods, and large smooth lanceolate or spathulate leaves.

The term 'woad' is derived from the Saxon 'wad,' which it has been suggested is derived from Woden, the Saxon God of War. It is synonymous with the Gallic *glastum*, with which, according to Pliny, the ancient Britons dyed their skin blue, in time of war and in connection with certain religious observances.

The plant is a native of Southern Europe, and from very early times it has been employed in dyeing blue, for which purpose, previous to the introduction of indigo from India, it was largely cultivated in various parts of Europe—*e.g.* Thuringia, Languedoc, Piedmont, &c. Its cultivation has now declined to such a considerable extent that in many districts where it used to be carried on extensively it is entirely extinct.

In this country, woad is now only grown, to comparatively limited extent, in the fen lands of Lincolnshire and Huntingdon. The seed is sown in the early spring, March, or April, and, the young plants having been duly thinned and weeded, the leaves are ready for the first plucking in June, which, at intervals of five or six weeks, is repeated once or twice, or as often as fresh leaves shoot up.

The newly-gathered leaves are at once crushed or ground in edge-runner mills to a pulp, which is then placed in small heaps to drain, till sufficiently dry to cohere and be submitted to the 'balling' process. This consists in working the pasty mass by hand into balls, four to six inches in diameter. These are at once spread out on wicker-work trays or 'fleaks,' and thoroughly dried in well-ventilated sheds. The balls are stored in a dry airy place till the whole crop has been gathered, and are then submitted to the so-called 'couching'—*i.e.* a fermentation process. For this purpose the balls are ground to a coarse powder, which is spread on the floor of the couching-house to a depth of two or three feet, and there reduced again to the consistency of a paste by frequent sprinkling with water and turning over with shovels. During this process, which lasts from twenty to forty days, the mass becomes heated and abundant offensive odours are given off. The operation needs to be conducted with some care and skill, so that the fermentation is neither so slow that a 'heavy' product is obtained, nor so rapid as to give one which is 'foxy.' When the fermentation has subsided, and the stiff, pasty mass is sufficiently cooled, it is packed in casks ready for the market.

It has been calculated that nine parts by weight of woad-leaves yield one part of the prepared product, and that this may contain at most 2 p.c. indigotin. Many samples of woad, however, contain little or no indigo.

Although woad was formerly used for the indigo contained in it and generated from the indican in the living plant during the couching process alluded to, it is at present only employed for the purpose of exciting fermentation in the indigo-vat ordinarily used by the woollen dyer, which is therefore termed the 'woad-vat.'

Spurious woad is sometimes prepared from the leaves of the rhubarb, cabbage, &c., but all such is accounted a very inferior ferment as compared with the true woad.

For employment of woad, *v.* Indigo.

Literature.—Chevreul, J. Ph. 1808, 66, 369; 1817, 350; A. Ch. 68, 284; Gilbert, Ann. 41, 245; 42, 315; Tromsdorff, J. Ph. 19, 93; Paris, Mus. Hist. Nat. Ann. 18, 251. J. J. H.

WOCHENITE *v.* Aluminium.

WÖHLERITE *v.* Cerium metals.

WOLFRAM, WOLFRAMINE, WOLFRAMITE, WOLFRAM OCHRE *v.* Tungsten.

WOLLASTONITE *v.* Calcium.

WOODBURYTYPE *v.* Photography.

WOOD GUM *v.* Gums.

WOOD APPLE GUM *v.* Gums.

WOOD NAPHTHA *v.* Wood, destructive distillation of.

WOOD OIL or **GURGUN** *v.* Oleo-resins.

WOOD'S ALLOY *v.* Tin.

WOODY NIGHTSHADE *v.* Dulcamara.

WONGSHY or **WONGSKY.** The Chinese name for the pods of *Gardenia grandiflora*, which contain large quantities of *crocin* from saffron. Dyes silks and wool a fine yellow without mordants; cotton must first be mordanted, best with tin. The colour of wongsky resembles that of annatto.

WOOD, DESTRUCTIVE DISTILLATION OF. In the selection of a wood for distillation regard must be paid to the age, hardness, percentage of moisture, as well as to considerations arising from the kind of wood employed and the part of the tree from which it has been cut. Old wood is darker than young, and after the wood is felled it grows also gradually darker on keeping, and wood is, as a rule, best if felled in the winter and allowed to season during the following summer before it is used for charcoal-burning or for distillation. Amongst *hard* woods are usually classed oak, elm, beech, and chestnut; the *soft* woods include pine, fir, poplar, lime, and willow; whilst the birch, maple, ash, larch, and alder occupy an intermediate position in this respect.

The specific gravity of a wood varies considerably, according to the age of the tree, the climate, and position in which it grows, the season of the year at which it is cut, and the part of the trunk selected. Nördlinger (Die techn. Eigenschaft d. Hölzer, Stuttgart, 1860) gives the following data:

Beech of	40	years' growth	0·770	sp.gr.
,,	13	,,	0·677	,,
,,	10	,,	0·412	,,
,,	5½	,,	0·368	,,

In the accompanying table are given:

(1) The average sp.gr. (Karmarsch, Handb. d. mechan. Technologie) of fresh and dried wood (1*a*) (1*b*).

(2) The percentage amount of moisture in fresh-cut wood (Schübler a. Harting, J. pr. 7, 35).

(3) The percentage composition of the organic portion of the different woods.

—	1*a*	1*b*	2	3		
				Carbon	Hydrogen	Oxygen and Nitrogen
Oak	0·973	0·785	35·4	50·0	6·1	43·9
Elm	0·909	0·619	44·5	50·2	6·4	43·4
Beech	0·980	0·721	39·7	49·5	6·1	44·4
Hornbeam	1·038	0·759	18·6	48·5	6·2	45·3
Chestnut	—	—	38·2	—	—	—
Birch	0·919	0·664	30·8	49·6	6·3	44·1
Planetree	0·893	0·681	27·0	49·8	6·3	43·9
Ash	0·852	0·692	28·7	—	—	—
Larch	0·809	0·519	48·6	50·1	6·3	43·6
Alder	0·901	0·551	41·6	49·1	6·1	44·8
Pine	0·908	0·613	39·7	50·7	6·2	43·1
Fir	0·894	0·600	37·1	50·9	6·3	42·8
Poplar	0·857	0·472	51·8	49·7	6·3	44·0
Lime	0·794	0·522	47·1	49·4	6·9	43·7
Willow	0·785	0·461	26·0	50·6	6·3	43·1

The amount of moisture is in general greater in soft than in hard woods, and this is clearly indicated by the numbers in the third column; it varies, of course, according to whether the wood is cut in the spring of the year or the autumn.

The *ash* left on combustion of wood may amount to as much as 5 p.c. of the weight of wood burnt, or fall as low as ½ p.c.; a little over 1 p.c. is about the average.

This ash contains potash, soda, lime, and magnesia in large quantities, chiefly in combination with carbonic acid, phosphoric acid, or sulphuric acid; also in smaller quantity manganese, iron, potassium chloride and silica.

If wood is directly extracted with water, there are dissolved out chiefly tannin, resins, and colouring matters, the cellular portion remaining varying according to the species of wood from which it has been obtained and the method of treatment to which it has been subjected. Essentially, the tissue may be looked upon as consisting of *cellulose* and a harder incrusting medium *lignin*.

General phenomena of distillation of wood. The dry distillation of wood commences at 100° to 130°C., the first products of distillation consisting almost entirely of water.

In ordinary distillation the temperature is allowed to rise gradually to 500° and then pyroligneous acid, wood spirit, &c., and uncondensible gases pass over; charcoal, some tar, and such non-volatile matters remaining behind in the retort. In the case of the distillation of wood in heaps (*meilers*) most of the products are wasted, whilst when the distillation is conducted in iron or brick ovens they can be recovered. The wood of trees of the conifer order yields more wood-tar and less pyroligneous acid than other kinds.

Some recent experiments carried out by A. Jakowleff (D. P. J. 264, 88, 128) give the following results as to the percentage of acetic acid yielded by different woods:—

Linden	10·20
Birch	9·41
Aspen	8·21
Oak	8·08
Pine	5·89
Fir	5·16
Birch bark	2·29
Cellulose, from birch	6·21
Cellulose, from pine	5·07

These numbers support the common opinion that conifers give a smaller yield of acetic acid than other woods. They also indicate that lignin is very productive, and that hard woods should be better than soft, although an exception to this occurs in the case of linden. Senff (B. 18, 60), from experiments of a more exhaustive character, draws similar conclusions. His results (somewhat abbreviated) are stated in the following table:—

Specimen of wood, calculated for 100 kilos	*	Total distilate — kilos	Tar — kilos	Pyroligneous acid		Anhydrous free acid — kilos	Charcoal — kilos	Uncondensed gas — kilos
				kilos	p.c. acid			
Carpinus Betulus—trunk	*a*	52·40	4·75	47·65	13·50	6·43	25·37	22·23
	b	48·52	5·55	42·97	12·18	5·23	20·47	31·01
Rhamnus Frangula — young trunks without bark	*a*	52·79	7·58	45·21	13·88	6·05	26·50	20·71
	b	45·38	5·15	40·23	11·16	4·49	22·53	32·09
Alnus glutinosa—trunk without bark	*a*	50·53	6·39	44·14	13·08	5·77	31·56	17·91
	b	47·76	7·06	40·70	10·14	4·13	21·11	31·13
Betula alba—trunk	*a*	51·05	5·46	45·59	12·36	5·63	29·24	19·71
	b	42·98	3·21	39·74	11·16	4·43	21·46	35·56
Sorbus Aucuparia—trunk	*a*	51·54	7·43	44·11	12·60	5·56	27·84	20·62
	b	46·40	6·41	39·99	10·41	4·16	20·20	30·34
Fagus silvatica—trunk	*a*	51·65	5·85	45·80	11·37	5·21	26·69	21·66
	b	44·35	4·90	39·45	9·78	3·86	21·90	33·75
Fagus silvatica—branches	*a*	49·89	4·81	45·08	11·40	5·14	26·19	23·92
	b	43·14	2·90	40·24	10·89	4·38	21·30	35·56
Populus tremula—trunk	*a*	47·44	6·90	40·54	12·57	5·10	25·47	27·09
	b	46·36	6·91	39·45	11·04	4·36	21·33	32·31
Quercus robur—trunk	*a*	48·15	3·70	44·45	9·18	4·08	34·68	17·17
	b	45·24	3·20	42·04	8·19	3·44	27·73	27·03
Pinus Abies—trunk	*a*†	45·37	4·42	40·95	6·66	2·73	30·27	24·36
	b	51·75	9·77	41·98	5·70	2·39	24·18	24·07
Pinus Abies—branches	*a*†	46·34	8·13	38·21	5·82	2·22	25·55	28·11
	b	43·85	5·44	38·41	4·20	1·61	23·35	32·80
Pinus Larix—trunk	*a*	51·61	9·30	42·31	6·36	2·69	26·74	21·65
	b	43·77	5·58	38·19	5·40	2·06	24·06	32·17

* (*a*) Slow distillation. (*b*) Quick distillation. † Not completely charred.

The products of distillation may be classified as follows:—

(1) *Non-volatile residue*—Charcoal (ash).

(2) *Volatile distillate.*

(*a*) *Condensible*—Water, pyroligneous acid, propionic acid, acetone, wood spirit, tar oils, tar, benzene phenol-guaiacol, cresol-phlorol, creosote, naphthalene, and paraffin.

(*b*) *Uncondensible*—Carbon monoxide, carbon dioxide, hydrogen, methane, ethane, acetylene, &c.

The wood tar and tar oils contain, amongst other products, iridol, citriol, rubidol, coridol, benzidol, benzene, toluene, xylene, cumene, eupion, creosote, mesite, xylite, paraffin, naphthalene, chrysene, pyrene, retene, pittacal, colophony, and resins.

The relative quality and quantity of these products depend also very largely on the temperature at which the distillation is conducted and the time occupied in the process.

At high temperatures more and more of the gaseous products are obtained, and less of the condensible products. If the distillation is allowed to proceed slowly, and with a gradual rise of temperature, the yield of carbon is greater (amounting to 24 to 30 p.c. as against 16 p.c.), but that of the volatile products is smaller than when the temperature is allowed to rise rapidly. This is due to the volatile products being in the latter case carried over rapidly and out of the reach of the dissociating influence of heat, whereas with a slow distillation they remain longer in the hot retort and are in part transformed into carbon monoxide, carbon dioxide, hydrogen, &c.

Under rapid heating, however, some of the tar is, as Pettenkofer observed, converted into hydrocarbons of the ethylene and acetylene series, and the resulting gases are no longer non-luminous.

Squibb, from experience in wood distilling in the United States, considers it not necessary to carbonise the wood, and finds that all the acetic acid can be got by heating at 160°C. to 200°C. with the production of little or no acetone. He uses retorts 20 feet long, 2 feet wide, and 10 feet deep, and heats by hot air. In the first 12 hours only water comes over, and in 24 hours the acetic acid begins to appear; the whole distillation extends over 6 to 7 days for each retort. When the heating is continued too long, smoke is given off and carbonisation of the wood sets in at the middle of the upper surface of the wood, extending downwards in a V-shape. The residue is an excellent fuel. From one cord of wood he obtains 1,200–1,400 pounds of liquid products, and in the case of oak 60–70 pounds of glacial acetic acid are contained in this.

Air-dried wood contains only some 40 p.c. of combustible matter, and completely dried 50 p.c. if we deduct the oxygen and its equivalent of hydrogen present in the wood. It follows, therefore, that very high temperatures cannot be attained by the combustion of wood, where so much heat is used up in the volatilisation of this water and other matters.

Where high temperatures are desired, the volatile constituents must therefore be previously got rid of in a separate operation. For this purpose the wood is charred by starting its combustion and then allowing only such a limited access of air that the combustion proceeds very slowly, and the heat generated is sufficient to drive off these volatile constituents. On the large scale this is done by stacking the wood together in a special manner in pits or in heaps (*v. Charcoal*, art. CARBON).

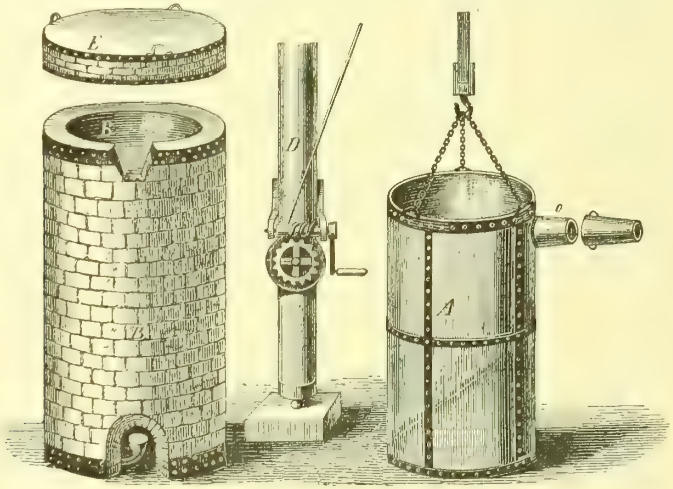

FIG. 1.

Distillation with recovery of products. Even where the volatile products of the distillation of wood are of primary, and the charcoal of secondary, importance, or of no market value, it is frequently the practice, at any rate in this country, to work up only a portion of the products, consisting of pyroligneous acid. The distillation of wood in mass is usually carried on in the neighbourhood of the source of supply, and the principal centre for this branch of the industry in this country is South Wales. It is carried out on a much larger scale in Russia, France, Germany, Austria, and in the United States. So far as the production of pyroligneous acid is concerned, the chief centres are situated in Yorkshire, Lancashire (chiefly spent wood), Gloucester, Derby, Somerset, and the vicinity of Glasgow and London.

In towns it is confined almost entirely to the spent woods (fustic, logwood, &c.) which can be had on the spot. In the former case the wood, cut into convenient lengths, is placed in cylindrical or oblong chambers of wrought or cast-iron, and heated externally, or in ovens with internal heating. Usually the cylinders, which are much used in France, are of strong iron-plate, 6 to 10 feet long, and from 3 to 4 feet in diameter. They are placed horizontally, like the retorts used in the manufacture of coal-gas, or are let down vertically into specially-constructed furnaces, in which they are heated. In this method of distillation at least two retorts are required for each furnace, one being heated whilst the other is being emptied and re-charged, and in this way considerable economy is effected in the working. As shown in fig. 1, the retorts are closed at one end and fitted at the other with a lid secured by a cross-bar. The volatile products pass off by a side-tube at the further end of the cylinder. Over the ovens are drying-chambers or floors, on which is spread the acetate of lime, the production of which is described later. By this arrangement the waste heat from the distillation process is utilised for the drying-chambers, with the further advantage that the gases pass away at the chimney at a moderate temperature. A further saving may be effected if the incondensible gases from the retorts are conducted through the fire and burnt, though in this case they should be previously passed through lime scrubbers. When the wood is small or of medium growth, the cylinder-oven may be advantageously replaced, as it is in South Wales, by square ovens, into which the wood is introduced in iron waggons (fig. 2) and the charcoal withdrawn without the breakage which is unavoidable in other methods of drawing the retorts.

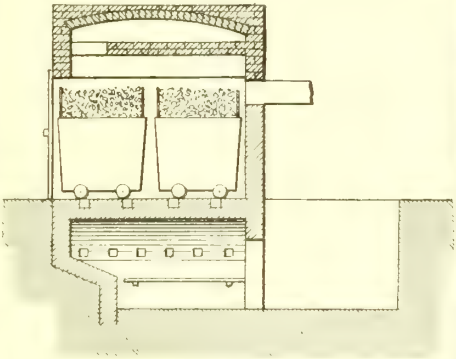
Fig. 2.

There are numerous advantages in this form of oven, and its only serious drawbacks are the liability to leakage through warping, and the difficulty of closing gas-tight. With this form of apparatus the moisture is first driven over at a gentle heat, and the condensers are then connected up and the distillation proper commences. The disposition of the retort and condenser is shown below (fig. 3). A is the retort in which the distillation is performed, the volatile products being carried off by the side tube A B to the condensers arranged in a vertical plane. The convolutions of the condenser are slightly inclined to the horizontal so that the liquid matters may pass downward and flow off into the acid well at E, whilst at D is seen a side tube by which the uncondensable products are carried away to the fire and burnt under the retort. Each limb of the condenser is surrounded by a water-jacket, the cold water from the cistern C entering at the lowest point near D, and running off at the highest point near B. In many works, however, such an arrangement of condensers is inconvenient, and in any case no sufficient range of pipes by which atmospheric condensation alone can be used is practicable. It is, indeed, most convenient in many cases to arrange the condensers underground.

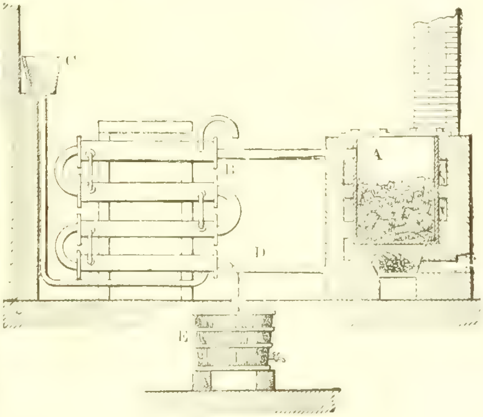

Fig. 3.

The condensers may be conveniently made so that at each bend there is a flange which can be readily removed for cleaning or in case of stoppage, and the condensers may be simply inclosed in a water tank. The accompanying figure shows another arrangement in common use in which the products pass directly from the ovens into the length of pipe A, from whence they must pass along the narrower copper pipes B C, the tank containing the pipes being filled with cold water.

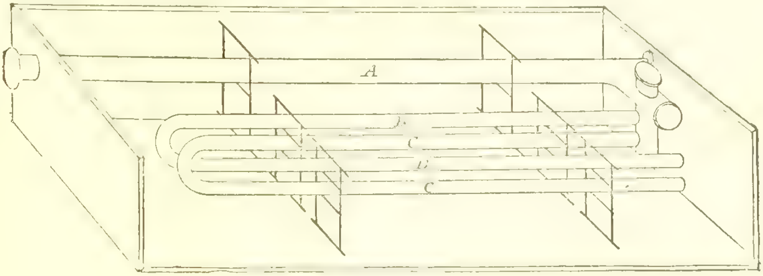

Fig. 4.

The yield of crude acetic acid with such retorts amounts to about 33 p.c. of the dried wood used, the charcoal being from 20–25 p.c., and the wood-tar 10 p.c., depending on the character of the wood. The process is especially suitable where the works are on a moderate scale, but is not economical for large works, though by having a series of retorts the working can be made continuous, and the fuel for heating is thus reduced to a minimum. In the case of retorts arranged horizontally (Chamotte retorts), special precautions must be taken against leakage, which is very liable to occur if the heating is carried out too rapidly. The distillation should occupy six to nine hours.

In *Russia* a somewhat similar form of plant is used, steam being blown through the cylinder at the commencement of the operation in order to heat up the wood more rapidly.

Turpentine and water form a large portion of the first distillate, and a rich acetic acid succeeds this. A more massive form is the *Reichenbach* oven. This is square (fig. 5), with double walls, the inner one being composed of refractory material, and the outer of ordinary brick. The space between these walls (about a foot wide) is packed with sand.

By means of the iron tubes within the retort the heat is brought into intimate contact with the wood. The volatile products are carried off by side tubes two feet in diameter, passing away from the sole of the furnace to the condensers.

The Reichenbach oven is, however, said to be wasteful and expensive in working, and hence has almost fallen into disuse.

The *Schwarz* oven does not essentially differ in character from the Reichenbach oven, though it is more carefully arranged for condensation and regulation of the temperature of carbonisation, and, indeed, charcoal of the best and most constant character is obtained from this furnace.

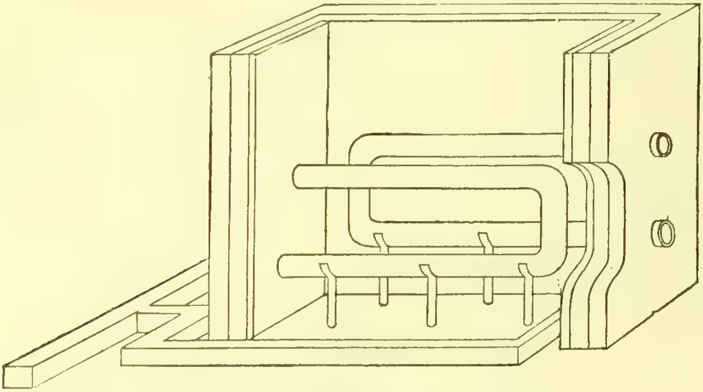

Fig. 5.

The *Hahnemann* retort (fig. 6) consists of a vertical tower 16 feet high and 8 feet wide, down the centre of which runs a wrought-iron tube, 1 to 1½ feet wide, serving the purpose of a chimney. The hearth is raised in the centre, and, after the wood is filled in, the top of the tower is closed with an iron lid and luted.

The vapours pass through perforations in the base of the central pipe, and the liquid products flowing to the edge of the raised hearth are carried off by a tube inserted in the base of the carbonising chamber. There is a side flue which is built up during the distillation, but opened when the contents of the oven are cool, for the purpose of withdrawing the charcoal. This retort gives a good yield of charcoal and of volatile products. Water is used for extinguishing and cooling the charcoal, and this product is, therefore, not a first-class quality. Much loss also occurs from exposure to the air which is necessary at intervals during the working of the charge.

The distillation process also proceeds very slowly, and, partly in consequence of the character of the structure, partly because of the cooling by water, the wear and tear in the oven is very great. It will not be necessary to describe the *Swedish* oven, as it differs in no essential particular from the form just described, except that there is no central chimney, and the carbonising chamber is shallower. The disadvantage is that unless the air supply is very carefully regulated to a minimum the process becomes a very wasteful one, since much of the charcoal and even of the products of distillation undergo oxidation. Stolze found that the products of distillation, per 100 parts of wood, with this form of retort, under the most favourable conditions, were:—

—	Charcoal	Gaseous products	Tar	Crude pyroligneous acid	Pure acetic acid
Birch *Betula alba*	22·4	22·0	8·6	45·0	4·47
Beech *Fagus silvatica*	24·6	21·8	9·5	44·0	4·29
Oak *Quercus robur*	26·2	21·7	9·1	43·0	3·88
Juniper *Juniperus communis*	22·7	20·8	10·7	45·8	2·34
Fir *Pinus Abies*	21·2	23·9	13·7	41·2	2·16
Pine *Pinus silvestris*	21·5	24·3	11·8	42·4	2·14

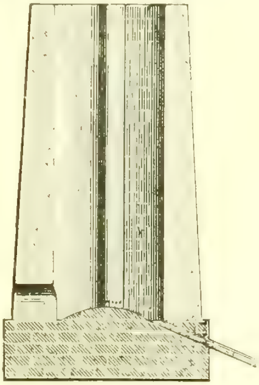

Fig. 6.

Distillation of spent woods. In this case the wood is already in a state of tolerably fine division, but before it is distilled, the moisture and various volatile foreign matters associated with it must be expelled. A convenient plant for dealing with spent woods is that patented by Halliday (fig. 7), in which the spent wood is fed at one end into a horizontal distillation chamber through a vertical tube, by means of an endless screw, and then slowly carried by a second screw at right angles to this, through the distillation chamber. The volatile products escape through an ascending flue, whilst the charcoal drops through at the extreme end of the chamber into water. A modification of Halliday's patent by Bowers has also come into use. In this there are two chambers of rectangular section side by side, the one being the drying chamber and the other the carbonising chamber. The carbonising chamber is heated from below by a furnace arranged as shown (fig. 8), whilst the drying chamber receives the heat from the furnace gases passing along the flue underneath it to the chimney. The spent wood is passed through fluted rollers and introduced on to the bed of the drying chamber by a hopper, the supply being regulated by a pair of rollers at the base of the hopper. Here it is spread out and carried along by transverse iron bars or scrapers (shown in the section, fig. 9), fitted on to an endless chain, the rate of which is also regulated.

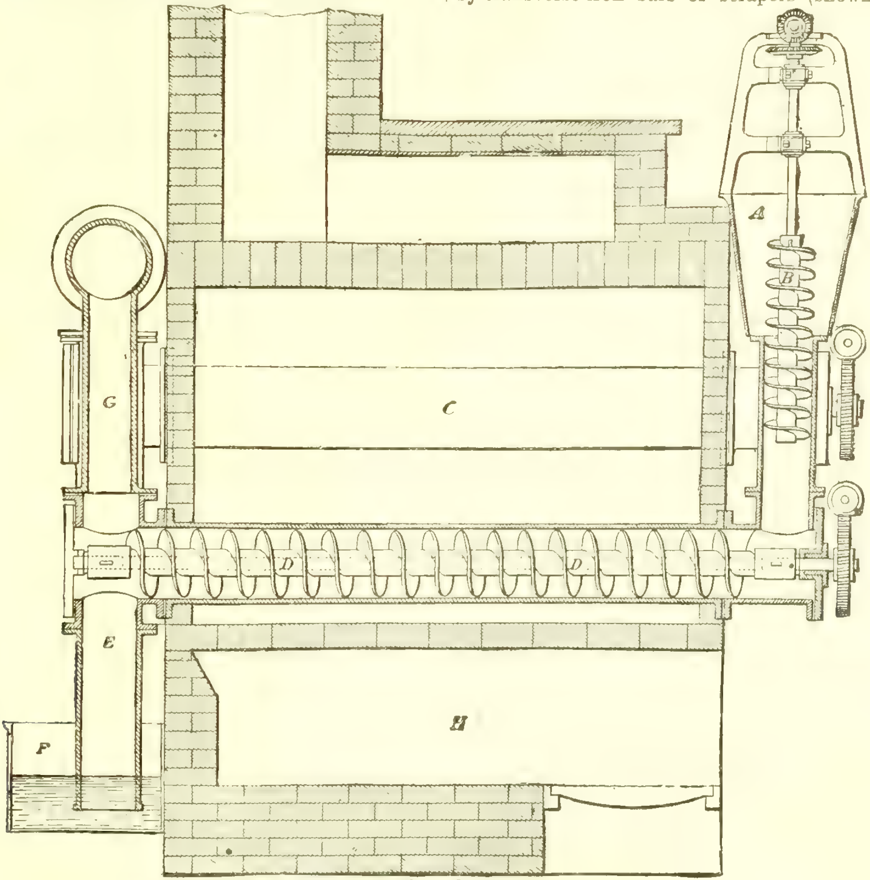

Fig. 7.

The wood being introduced at the end nearest the chimney, is gently heated, the temperature to which it is exposed increasing as it advances along the bed of the chamber. By the time it has passed through the drying chamber, the wood is almost perfectly free from adherent moisture, and it is now introduced by means of a hopper (D) into the second chamber, the arrangement of which is similar to the first, except that flues are provided for carrying off the volatile products to the condensers, as shown at G G. In this chamber the temperature is sufficiently high to expel the whole of the volatile matters, and there is discharged, at the end near the furnace, the residual charcoal, which is run into a box and removed at intervals. Such a plant will run continuously with little attention, and can be very economically worked in districts where a ready supply of spent wood is at hand. The charcoal obtained is often a drug on the hands of the distiller. It is, however, now largely used for packing the meat refrigerators in ships. The distillate obtained is of a more complex character than that from fresh wood, and is more difficult to work up, especially if it is sought to recover other products than the pyroligneous acid.

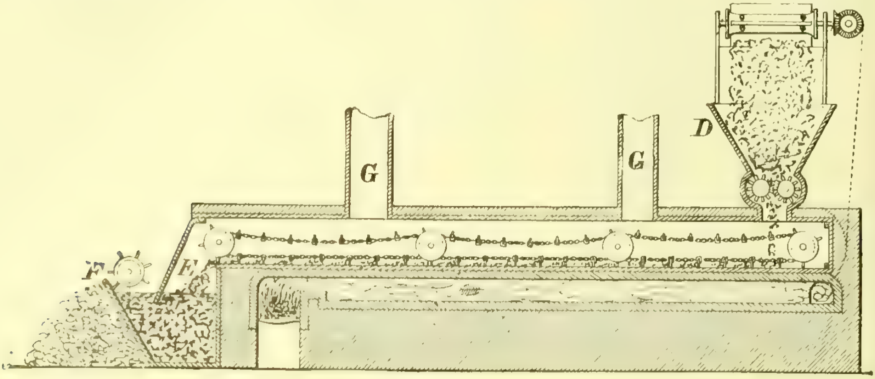

Fig. 8.

Distillation by steam. This method was first applied on a large scale by Violett, for obtaining charcoal of a constant character which will ignite readily, such a product being especially adapted for the manufacture of gunpowder. The apparatus consists of two concentric wrought-iron cylinders, the steam being admitted into the space between the cylinders.

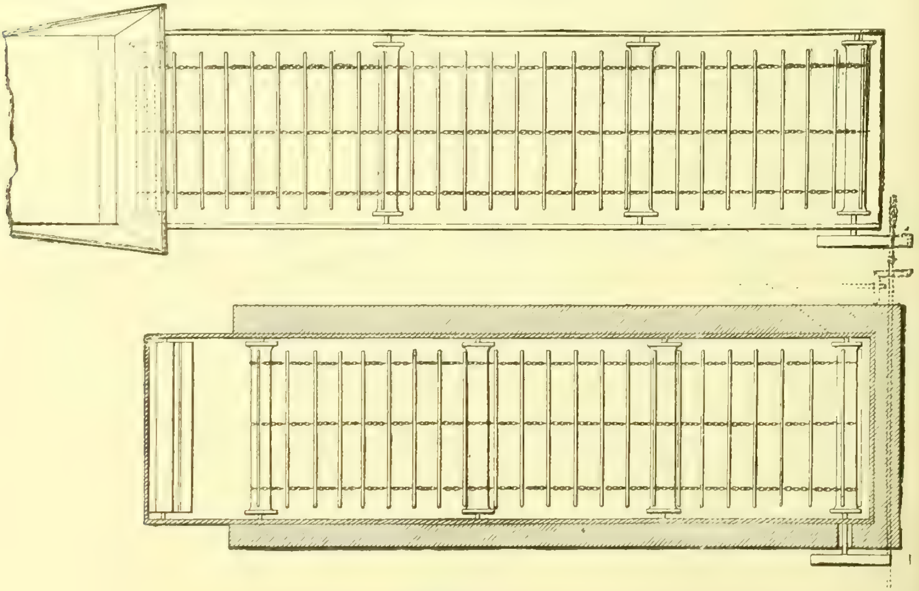

Fig. 9.

The black alder used for this special kind of charcoal is introduced into the inner cylinder, which is then closed air-tight, and the heating is continued so long as empyreumatic vapours come over. The yield of charcoal amounts to about 30 p.c. of the air-dried wood.

Some forms of apparatus are, however, in use where steam is admitted directly to the carbonising chamber, and the distillation performed in this way. All such processes, however, render condensation very difficult, and the pyroligneous acid obtained is much more dilute, of course, than that from dry distillation. The process of distillation of such a product for acetic acid is also more difficult, and Steedman has proposed the use of paraffin or some similar substance in such a case. The impure acid is passed into a rectangular copper vessel divided by partitions slightly inclined from the horizontal, and attached at one end of the vessel, a free space being left at the other.

The gases, being introduced at the bottom of the tank, travel along the underside of these partitions in turn, finally passing out at the surface. The paraffin is heated by means of a steam jacket or coil, to a temperature a little higher than that at which the acid condenses. Most of the resinous matters and impurities which are most difficult to separate in the ordinary process of purification are retained, but the outlay on the purifying agent is a large one, and the recovery of the paraffin is difficult. The method is therefore open to objection, and a simple and direct method of purifying the dilute crude acid is still a desideratum. The crude liquors are allowed to stand twenty-four hours, so that the tarry matters may separate out. If they can then be run off and subjected to a second agitation and settling, so much the better. They are now subjected to distillation in copper or cast-iron stills under the action of direct heat, or by steam-coils at 20 to 30 lbs. pressure; the spirit[1] passes over first and is collected in a separate receiver from the acid. The tarry residue is distilled to a pitchy consistency and then a fresh charge introduced; the tar is only run off when it has accumulated to the depth of about 2 feet, which occurs after ten to twelve charges have been worked off. The tar is then tapped whilst still hot.

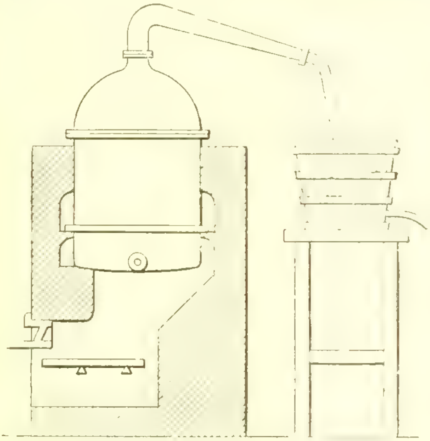

FIG. 10.

The better classes of *acetic acid* used in the arts are obtained by redistillation of certain acetates with mineral acids.

Acetate of soda is largely used for this purpose, though lime or lead salts may be employed. The acetate (100 parts) is introduced into a copper still (figs. 10 and 11) along with sulphuric acid diluted with three times its amount of water (60 parts) and mixed with pyrolusite (5 parts), this being added to prevent the formation of sulphurous acid during the process of distillation. The distillate is condensed by passing through an earthenware worm, the receiver being changed when empyreumatic vapours begin to come over. The part which now passes over is subjected to a second distillation and then contains about 35 p.c. of anhydrous acetic acid.

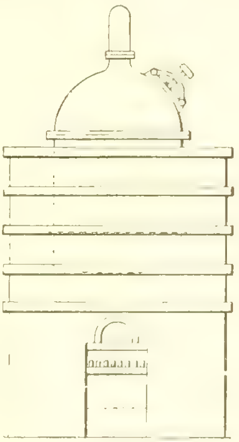

FIG. 11

If the distillate is not quite colourless it may be treated with animal charcoal or beechwood shavings. If glacial acetic acid is wanted it is necessary to redistil over fused calcium chloride, the distillation being repeated till the whole of the acid crystallises below 15°C.

The sulphate of soda left in the still can be disposed of to the alkali-maker. The ordinary brown acetate of lime distilled in the same way gives a very concentrated acid if the impurities which pass over with the first fraction are removed by a further distillation with sodium bicarbonate, though no practicable process is known for obtaining pure acid in this way. Hydrochloric acid is used in place of sulphuric in order to avoid the formation of sulphate of lime, which is very objectionable for the still.

A concentrated and pure acetic acid is obtained by the dry distillation of acetate of copper in glass or earthenware retorts; the product mixed with certain essences constitutes what is known as aromatic vinegar or the *vinaigre des quatre voleurs.*

By Condy's process, which has been adopted at Newcastle-on-Tyne for the production of acetic acid from the brown acetate of lime, crystals of calcium acetochloride ($CaCl_2.Ca(C_2H_3O_2)_2.10H_2O$) are prepared by mixing solutions of calcium chloride and calcium acetate, and this product is finally distilled with mineral acid in the ordinary manner.

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[1] Sometimes both are collected together and the spirit not distilled off until after neutralisation of the acid with lime. In this case the spirit is less contaminated with tarry oils.

The acetates. The acetic acid obtained by these processes retains traces of the crude pyroligneous acid, which give it a characteristic odour and slight colouration. If desired, these impurities may be removed by redistillation in glass vessels after the addition of 0·5 to 1 p.c. of bichromate of potash. In addition to the methods of distillation and of refrigeration, &c. (*v.* ACETIC ACID), glacial acetic acid may be obtained by adding strong acetic acid to acetate of potash sufficient to convert it into the acid salt. This is then warmed in a tubulated retort; the weaker acid passes over first, and when the thermometer rises to near 300°C. the receiver should be changed, and the glacial acid passes over.

The temperature should not be allowed to rise above 300°C.

The acetates, which are usually prepared on the large scale from pyroligneous acid for use in the arts, are:—

Acetates of alumina (red liquor),
,, iron (black liquor and iron liquor),
,, lead (sugar of lead),
,, lime (grey and brown acetates),
,, soda,

and also on a smaller scale the acetates of tin, copper, and zinc.

Red liquor. This is made by the addition of acetate of lime or lead to sulphate of alumina or alum. The advantages of acetate of lead over acetate of lime are:—

(*a*) The acetate of lead is less variable in composition.

(*b*) The sulphate of lead precipitated is less bulky and the mordant more easily washed out, giving less loss and a smaller quantity of weak liquors to be worked up. In any case it is desirable that the lime salts used should be as pure as possible, and all the ingredients must be free from iron or copper, which act most prejudicially in the mordanting process.

The stability of the liquors is not great, and hence they ought to be used as soon as possible after their production. A mordant which gives good results with alizarine colours may be prepared by dissolving freshly precipitated alum in acetic acid.

Acetate of lime. This product is manufactured in three forms:—

(*a*) Brown acetate (60–70 p.c. acetate); (*b*) grey acetate (80–85 p.c. acetate); lime liquor, containing about 10 to 15 p.c. of acetate of lime along with 7 or 8 p.c. of impurities, such as sodium and calcium chlorides and tarry residues, the rest being water.

Naphthas. In the preparation both of the grey and brown acetate, naphtha is recovered—that from the brown acetate being the *miscible wood naphtha*, and that from the grey acetate the *solvent naphtha*. The former is run over into a cast-iron pan, redistilled and condensed in a copper worm, the distillation being repeated in copper stills, preferably with steam-jackets or steam-coil, till it reaches 60° over proof.

The *solvent naphtha* is usually only worked up to from 30° to 45° over proof, and is used for dissolving resins and gums.

Wood spirit. On neutralising with lime and distilling, the first part of the distillate consists of naphtha, and this should be collected until a sp.gr. of 0·99 to 1·00 is indicated. At this sp.gr., or when a sample thrown on hot cinders (the rough commercial test) no longer inflames, the receiver is changed, and the acetic acid collected. The first distillate is dark brown in colour, and has a strong odour of wood oils, &c. It contains in addition to methyl alcohol, methyl acetate, dimethyl acetate, acetone, ammonium acetate, amines, and tarry matters. If distilled over lime some of these impurities are retained by the lime, whilst others are decomposed. Such a process, however, does not get rid of ammonia or volatile alkaloids, which are often present in some quantity. These may be best removed by distilling the crude wood spirit alone, or better if 2 to 3 p.c. of sulphuric acid be previously added to it. Benzol or other hydrocarbons may be washed out with water, when they rise to the surface in a layer from which the spirit can be run off by means of a separating funnel.

In such distillations the liming must be carefully managed, since if underlimed, the rivets and joints of the still are attacked and leakage is sure to ensue sooner or later, whereas, if overlimed, a tough sediment may be deposited, and the liquor tends to prime over into the condenser. The weak naphtha distillate from the 'wash boiler' or No. 1 still is concentrated by passing through a series of stills (generally four) diminishing in capacity. In case of overliming also, ammonia comes over and the condenser or stills are attacked if they are of copper. In this case it is best to use wrought iron or cast iron for the first one or two stills (Morgan, S. C. I. 1885, 730). The wood spirit is now treated with calcium chloride, with which the methyl alcohol enters into combination. The compound so formed is not decomposed, even at 100°C., and the remaining impurities are distilled off at this temperature, the methyl alcohol being finally obtained by heating the calcium chloride compound with water. The wood spirit so obtained is largely used for methylating spirit, and for this purpose must be at least 60 o.p. (Sykes), and should give rise to no turbidity when water is added to it. It is also used in varnish and finish manufacture, and the fractions rich in acetone are especially valuable for this purpose since they dissolve gums more readily than the pure spirit. It is also used in the production of aniline colours. Fawsitt (S. C. I. 1885, 319) criticises the system of estimating the value of wood spirit by Sykes's hydrometer tables, not only because of the variations (not great, however) between the density of this spirit and of ethyl alcohol, for which these tables were constructed, but especially since good tables for methyl alcohol are obtainable. Sykes's tables also run only as high as 93 p.c., whereas methyl alcohol is sold of a higher strength than this. In his opinion it would be far preferable that the strengths should be stated according to percentages, and not in Sykes's formula.

Acetone occurs amongst the products of the dry distillation of wood, and is formed also when acetic acid is passed through a tube at a dull-red heat. It can be rectified on a water bath over quicklime till it shows the proper boiling-point (55·6°C.). When calcium hydroxide or calcium chloride are added to a mixture of acetone and water, the acetone separates, and, if in sufficient quantity, it forms a crystalline compound with calcium chloride.

Methyl acetate is associated in the products of distillation with wood spirit, and is obtained from this body by treatment with finely-powdered calcium hydrate. The crude acetate is freed from resins and colouring matters by adding alum, which throws down the lime as sulphate, and also alumina, carrying these impurities with them.

It is then filtered through charcoal, and dried by distillation over calcium chloride, which, at the same time, removes any methyl ether which is present. Methyl acetate is a colourless liquid of sp.gr. 0·9562, boiling at 50°C. and miscible in all proportions with water, alcohol, and ether. It frequently contains free acetic acid.

Wood-tar. Wood-tar is a thick, dark-coloured, viscous material, still acid from the presence of some acetic and other acids, and possessing a specific gravity of about 1·05 to 1·15. The acid is removed by neutralisation with milk of lime, the soluble acetate of lime being washed out and recovered, the residual tar being then subjected to further treatment as described hereafter.

Tars obtained from different centres of industry show considerable variations in colour and in viscosity, and also in respect of the amount of ethereal oils and resin which they contain.

The character of these variations is proximately indicated in the following table:

—	Acetic acid	Light oils	Heavy oils	Pitch	Gas and loss by distillation
'Meiler' tar from South Austrian black fir, sp.gr. 1·075	20 parts	10 parts sp.gr. 0·966	15 parts sp.gr. 1·014	50 parts	5 parts
'Meiler' tar from Bohemian pine, sp.gr. 1·116 . .	10 parts	5 parts sp.gr. 0·977	15 parts sp.gr. 1·021	65 parts	5 parts
Retort tar from Salzburg, sp.gr. 1·18 . . .	10 parts	10 parts sp.gr. 1·012	15 parts sp.gr. 1·022	55 parts	10 parts
Tar from distillation process by superheated steam .	5 parts	20 parts sp.gr. 0·920	25 parts[1] sp.gr. 0·978	30 parts	5 parts

[1] Also 15 parts of oil containing paraffins.

The tar obtained by distillation from retorts contains less resins and creosote and more paraffin than that from the distillation in heaps, whilst the product of distillation by superheated steam is characterised by a low percentage of pitch and a high yield of paraffin. Wood tar is used for creosoting wood, for roofing felts, and as an antiseptic.

The recovery of tar oils from wood-tar. For this purpose the tar is subjected to distillation in cast-iron or wrought-iron stills. For small works the cast-iron stills are to be preferred to the wrought iron, especially as they admit of the distillation being carried further, and the residue is more readily removed. The stills are sometimes 12 to 15 feet in diameter and 10 to 12 feet high, and are of the form of an upright cylinder with a spherical head. They are fitted inside with a stirrer, and carrying at its upper part a grid which serves to break the surface of the tar, and prevent its boiling over. A side tube is provided for filling in the tar, and at the bottom is also a tube for running off the residual pitch at the end of the distillation. The whole is inclosed in a jacket of stone so as to prevent cooling by radiation as far as possible.

The heating is done with caution, and the whole period occupied in the distillation is about five or six hours on an average. After the water has been got rid of, there passes over an oil of sp.gr. 0·96 or thereabouts, which turns slowly brown on exposure to air. Then follows a heavier oil of sp.gr. 1·014 and of a yellowish-green colour. These oils constitute about 10 and 15 p.c. respectively of the whole. The *light oil* is worked up in the following manner. It is redistilled from the brown resinous bodies, which have formed by oxidation, the still used being higher than that already described, so that only the more volatile portions pass over. The distillate is treated with soda-lye to remove creosote and redistilled, this treatment being repeated several times. Ultimately a mobile, colourless, highly refracting oil is obtained, which when fractionated, passed over between 47°C. and 165°C., having a specific gravity of from 0·660 to 0·985. The first portion resembles Reichenbach's *Eupion*, and is almost as volatile as ether, whilst the portion passing over at 60°C., and having the sp.gr. 0·800, is similar in character to *mesite.* The oils distilling below 70°C. seem to form a series resembling in some degree the benzene hydrocarbons, and their nitro derivatives can be reduced with iron filings and transformed into colouring matters. Schweitzer from crude-wood spirit obtained in a similar way *mesite*, and also a fraction boiling at 61·5°, sp.gr. 0·816, which he called *Xylite.* It ought to be mentioned that wood-tar, however well it is settled, contains about one-third of pyroligneous acid, which is recovered by distillation, and worked up with other portions of this product.

Treatment of the heavy tar oils. Recovery of creosote. Carbonate of soda is first added for the purpose of neutralising any free acetic acid which may be present, and the oil is then run off from the liquid and well shaken with soda-lye (sp.gr. 1·20).

The oil remaining is rectified, and this treatment with soda-lye and rectification repeated several times.

The lighter oil is finally collected separately from the heavier, which contains most of the paraffins.

This heavier oil is kept in a cool place till the paraffin crystallises out; the residual oil after the removal of the paraffin consists to a large extent of *Xylol*, but contains also *Eupion* and *Kapnamor*. The alkaline liquors which have been collected from time to time contain the *creosote*, and this is separated again by neutralising these liquors with sulphuric acid and subjected to fractional distillation, the first and last portions of the distillate being rejected. Any acid still remaining may be removed by treatment with carbonate of soda and traces of resinous matters by distillation with sulphuric acid and bichromate of potash. The creosote so obtained is a colourless, highly refracting oil, of sp.gr. 1·04, boiling at 208°C. It is only slightly soluble in water, but dissolves readily in ether or alcohol. Wood creosote differs in many of its reactions from coal-tar creosote. On adding to the latter (15 parts) collodion (10 parts) the whole becomes gelatinous, whereas wood creosote gives a clear solution with collodion. Neutral ferric chloride gives a green colouration gradually turning brown with wood creosote, phenol yielding a purple colouration.

Reichenbach separates creosote from acetic acid by shaking it with Glauber's salt, when a brown oil separates on standing.

This is treated with potassium carbonate and distilled with water, resinous matters are thrown out and a clear yellowish oil passes over. This is treated alternately several times with phosphoric acid and soda-lye; *Eupion* rises to the surface. The creosote may be obtained by the method stated above, viz. treatment of the alkaline liquors with sulphuric acid and the purification by washing and distillation is repeated until the soda-lye is not coloured. The creosote obtained by Reichenbach boils at 203°, and has the sp.gr. 1·037. It contains, however, guaiacol and creosol.

Recovery of Eupion. This product accompanies the creosote and paraffin fractions, the crude oil being treated with caustic potash to remove the former, whilst the latter is separated by repeated distillation. It is a pleasant smelling colourless liquid of sp.gr. 0·740, boiling at 47°C., and volatilising slowly at ordinary temperatures. It is insoluble in water, and not readily soluble in alcohol or ether; it dissolves resins to some extent, but on warming, caoutchouc dissolves freely in it.

Recovery of kapnamor. Only the oils which are heavier than water are used for the preparation of this product. These are shaken with caustic potash solution of sp.gr. 1·20, and the part which remains undissolved is put on one side. The solution in alkali is boiled some time and then treated with sulphuric acid. The oil which separates is then made alkaline with potash and distilled, the distillate being treated with a somewhat weaker solution of potash and with sulphuric acid repeatedly till no more of the oil separates out. The creosote is in this way removed and the oil residues contain the kapnamor. These are after further treatment with potash dissolved cautiously in fuming sulphuric acid, any oil which remains undissolved being eupion. After standing some time this is diluted with water, neutralised with ammonia, and distilled. Ammonia liquor passes over first, and then *kapnamor* combined with ammonium salts, which it retains with considerable avidity. This part of the fraction is distilled with caustic potash, and the oil, of sp.gr. 0·98 and boiling-point 185°C., is collected. It can be rectified over chloride of calcium. Kapnamor is a highly refracting colourless liquid of agreeable odour, which, when rubbed on the hands, reminds one of ginger. Like the previous oils, it is inflammable. It dissolves freely in alcohol, ether, turpentine, &c., and is a solvent for paraffin, naphthalene, stearin, and for many resinous substances. Like eupion it dissolves caoutchouc if warmed, whilst in the cold it causes it to swell up and only dissolves it very slowly.

Recovery of picamar. This body was also first prepared from wood-tars by Reichenbach. It separates out in crystals as a potash compound from the alkaline liquors. The crystals are treated with acid which separates the picamar, further purification being effected by distillation. It is a colourless oil of sp.gr. 1·10, boiling at 270°C. It is only slightly soluble in water, but readily in alcohol, ether, and wood-spirit. It dissolves resins, but not caoutchouc.

Products of less importance are *cedriret*, which is recovered by distillation from a portion of the alkaline extract neutralised with acetic acid, and *pittacal*, which is separated out by the addition of baryta. For further details a most interesting contribution by Schorlemmer (History of Creosote), Cedriret, and Pittacal (S. C. I. 1885, 152) may be consulted.

Recovery of the paraffins &c. When the wood-tar residues are distilled further, the products obtained consist for the most part of chrysene and pyrene. These bodies are separated by treatment with ether in which only pyrene dissolves. *Chrysene* is a yellowish crystalline substance which melts at 230° to 235°C., and boils with partial decomposition. The composition usually assigned to it is $C_{18}H_{12}$; it occurs also amongst the products of destructive distillation of coal.

Pyrene ($C_{16}H_{10}$) can be crystallised from alcohol or ether. It melts at 170–180°C., and can be distilled without decomposition.

Paraffin ($C_{20}H_{42}$). The crystals which have already been spoken of are separated from the oil accompanying them by means of a centrifugal machine, and then subjected in cloths to hydraulic pressure. The paraffin thus obtained is treated with sulphuric acid, and then finally washed well with water, any traces of acid still retained being neutralised with alkali. To get it quite clear the paraffin is melted with 2 p.c. of stearin and saponified with caustic soda and allowed to settle. The final stage of purification may, if preferred, be carried out by washing with benzene, pressing, and then exposing to superheated steam. In this way the paraffin obtained is of a fine character, though there is more loss in paraffin than by the first method.

The paraffin obtained from wood-tar has the sp.gr. 0·870, and melts at 44 C. It burns with a wick, and is used for making candles. It is very indifferent towards reagents, and is not acted on by chlorine, by mineral acids, or by alkalis at the ordinary temperature. It is insoluble in water, and not freely in alcohol; ether and ethereal oils, however, dissolve it readily.

The Resins. These occur in smaller quantity along with the heavy and light oils, but for the most part distil over after them. They are readily soluble in alcohol and ether, and readily form condensation products, taking up oxygen.

Wood-pitch. The residue left in the still is mixed, by means of the stirrer, with 20 p.c. of colophony asphalt, or with 50 p.c. of coal-tar, and sent into the market for use in shoemaking.

Determination of acetic acid in sodium acetate. Squibb recommends, for the purpose of determining the acetic acid in sodium acetate, the distillation of 10 grms. of the acetate in a glass retort, with the addition of 20 c.c. of water and 10 c.c. H_2SO_4. 15 c.c. are distilled over, and then the distillation is interrupted and 20 c.c. more water added to the residue. 10–15 c.c. are now distilled over, and when this is again repeated the whole of the acetic acid will be found in the distillate.

The valuation of brown and grey acetates of lime. Two methods are in use: (*a*) The amount of lime salts soluble in water is determined, and the acetic acid calculated from this on the assumption that all the lime salts soluble in water consist of calcium acetate. This is a very crude method, since caustic lime is dissolved, and if the acetate has been overheated (frequently the case) this is a factor that cannot be overlooked.

Then, again, there may be present lime salts of other organic acids (especially in the case of salts prepared from spent woods), though these are liable to occur in smaller quantity, where the better methods of manufacture now known are employed. The better the sample of acetate the less is the error which is likely to arise from this rough method of analysis. The distillation method, known in America as the *English commercial test,* is now largely used in place of this.

(*b*) *Methods based on distillation.* For this purpose, hydrochloric, sulphuric, or phosphoric acid may be used.

(1) *Hydrochloric acid is used.* In this case an error is liable to occur through the volatile hydrochloric acid being carried over with the acetic acid, and for a correct estimation the amount of this must be determined in the distillate and deducted. The advantage of using hydrochloric acid is that it does not act on organic matter which may be present, and that, as the calcium chloride formed is readily soluble, the distillation can be carried to an extreme limit with safety.

(2) *Sulphuric acid is used.* In the use of this acid there are three disadvantages. The acid concentrates in the retort as the distillation proceeds, and acts on the organic matter present, giving rise to sulphurous acid, which is carried over, and adds to the acidity of the distillate. This may be avoided by distilling in a current of steam (American Chemist, 6, 294). Secondly, the calcium sulphate formed is very troublesome and gives rise to bumping, though this also is avoided if steam is used for distillation. Thirdly, if chlorides of calcium or sodium be present, hydrochloric acid is carried over with the distillate. The addition of silver sulphate before the distillation commences, however, will overcome this.

(3) *Phosphoric acid is used.* This is perhaps the best and most reliable reagent to use in such determinations, the advantages being:—

(*a*) It does not act on the organic matter.

(*b*) During the process of distillation the bulk of the liquid is not allowed to fall below 15 c.c., and the sodium chloride or calcium chloride that may be present hence does not undergo decomposition.

(*c*) It forms a clear solution with acetate of lime, if at least five times the weight of glacial phosphoric acid is used as of the acetate taken.

The phosphate of lime dissolves up in this excess, and there is no trouble from bumping. Distillation by steam must be employed, and the phosphoric acid should be previously tested for the presence of volatile acids, such as nitric, which might distil over. The analyst should also satisfy himself (molybdate test) that no phosphoric acid has been carried over. As indicator, phenolphthalein is to be recommended. In any case, buying according to the acetic acid estimation should be insisted on, instead of the older and widely practised method of merely determining the amount of salt soluble in water.

G. H. B.

WOOD-CLOTH. Mitscherlich has applied the bisulphite process to wood for the production of a fibre which can be spun. Thin boards, free from knots, are cut into strips in the direction parallel with the grain, and are then boiled with a solution of sulphurous acid or alkaline bisulphite. The wood after boiling is partially dried in the open air or in drying-rooms, to strengthen the fibre, which is originally very weak and tends to break with the slightest strain, but on drying becomes comparatively strong, and does not resume its very breakable condition on the addition of water. The damp masses on the frames are transferred on a travelling endless cloth to a pair of rollers, which may be plain or corrugated. Cutting of the fibre by the corrugations is prevented by passing the endless cloth over the lower roller and covering the upper one with canvas. The pressed masses are passed through other rollers, preferably to the number of six pairs. By the continued treatment the fibre becomes so pliable and separated that they may be employed directly for coarse filaments. For obtaining a perfect separation of the fibres without material deterioration, the boiled and pressed masses must be completely dried and then combed in a manner similar to the combing of flax and cotton, but with the difference that the pins of the combing machine must be very strong. The separation of the extractable matter from the fibre produced by the boiling can be effected at any time, but preferably after the fibre has been spun into threads (Eng. and Min. Journ. 47, 215; S. C. I. 388).

WOOD-PITCH, WOOD-SPIRIT, WOOD-TAR, *v.* WOOD, DESTRUCTIVE DISTILLATION OF.

WOOD TIN (*Native oxide of tin*) *v.* TIN SALTS AND OXIDES.

WOOL. This epidermal excrescence is of the type of horny tissues, and springs out of subcutaneous follicles. Some naturalists have distinguished only three distinct varieties of wool-bearing *ovis*; others, many more. Whatever the number of varieties may be, it is indisputable that the character of wool varies greatly in straightness, length, and fineness, not only in so-called different kinds of sheep, but in the same kind under unequal conditions of soil, climate, and selection.

The typical wool-fibre is always covered with scales, similar to those inclosing human hair, but freer in their attachment to the fibre and somewhat pointed at the upper edge. No difference can be distinguished as to the inner fibre between wool and hair. These scales, however, are found to exhibit a wide difference in number, strength, and distribution in various examples of wool. The length of fibre may be taken to range from an inch or so to as much as a yard, and the diameter may be from 1-3500th to 1-50th of an inch. Dr. F. H. Bowman constructed an apparatus for determining the relative strength of fibres, from which he ascertained the breaking strain of different wools, taking the average of five filaments of each, and expressing the power in grains to be:—human hair, 1,641; Lincoln wool, 502; Leicester wool, 473; Northumberland wool, 429; Southdown wool, 86; Australian merino, 50; Saxony merino, 39; mohair, 586; alpaca, 149. Generally speaking, the strength increases with the diameter.

According to Mulder, the average composition of horny tissue is:

Carbon	50·54 p.c.
Hydrogen	6·91 ,,
Nitrogen	16·83 ,,
Oxygen	22·07 ,,
Sulphur	3·65 ,,

Composition of Wool Fibre (Bowman).

—	Lincoln wool	Irish wool	Northumberland wool	Southdown wool
Carbon .	52·0	49·8	50·8	51·3
Hydrogen .	6·9	7·2	7·2	6·9
Nitrogen .	18·1	19·1	18·5	17·8
Oxygen .	20·3	19·9	21·2	20·2
Sulphur .	2·5	3·0	2·3	3·8
Loss . .	0·2	1·0	—	—
	100·0	100·0	100·0	100·0

In this series the loss estimated in the first two analyses appears to represent the amount of mineral ash which in the last two is estimated along with the carbon. Chevreul found the mineral matter in wool to amount to from 1 to 2 p.c.

Wool treated in turn with hydrochloric acid (0·13 p.c. acid), anhydrous ether, and alcohol is freed from all soluble matter, the sweat being taken up by the water, the suint or yolk by the alcohol, and the fat by the ether.

E. J. Mills considers that the summary of analyses of wool contained in Gmelin's 'Handbook of Chemistry' warrants the conclusion that wool is a definite chemical compound, known as keratine $C_{42}H_{157}N_5SO_{15}$ (C. J. 43–142).

From the decomposition of scoured wool by a solution of barium hydrate, Schützenberger obtained the following result:

Products of Decomposition of Wool.

Nitrogen (as ammonia) . .	5·25
Carbonic acid (as $BaCO_3$) . .	4·27
Oxalic acid (as BaC_2O_4) . .	5·72
Acetic acid	3·20
Pyrolene and volatile products,	1 to 1·50
Elementary composition of fixed residue, containing leucine, tyrosine, and other volatile products	C. 47·85
	H. 7·69
	N. 12·63
	O. 31·83
	100·00

Analysis of ash of Lincoln wool (Bowman).

—	Whole ash	Soluble ash	Insoluble ash
Potassium oxide K_2O . .	31·1	42·3	trace
Sodium oxide Na_2O . .	8·2	17·3	trace
Calcium oxide CaO . .	16·9	4·5	51·2
Alumina Al_2O_3 . .	12·3	3·6	37·7
Ferric oxide Fe_2O_3 .			
Silica SiO_2	5·8	4·1	11·1
Sulphur trioxide SO_3 . .	20·6	24·8	trace
Carbon dioxide CO_2 . .	4·2	3·4	—
Phosphorous pentoxide P_2O_3.	trace	trace	trace
Chlorine	trace	trace	—
	100·0	100·0	100·0

In this instance 1 p.c. of ash was obtained by burning wool, previously scoured with hard white curd soap, thoroughly washed and dried. On treating the ash with water, 75 p.c. dissolved, leaving 25 p.c. insoluble.

Sheep's wool dried at 40° contains about 1·5 to 3·5 p.c. of sulphur. Chevreul concluded that, since the wool disengages sulphur and hydrosulphuric acid without losing its characteristic structure, the sulphur enters into the composition of a body distinct from the filamentous material proper. He found even the repetition 48 times, for 48 hours each time, of the treatment of wool with milk of lime, dilute hydrochloric acid, and water in succession does not entirely remove the sulphur.

Faist determined the amount of suint and fatty matter to be from 21 to 27 p.c. in washed and about 44 p.c. in unwashed wool. With regard to suint, Youatt says: 'From its adhesiveness and colour it is called the yolk. It is found in greatest quantity about the breast and shoulders, the very parts that produce the best, and healthiest, and most abundant wool; and, in proportion as it extends in any considerable degree to other parts, the wool is there improved. It differs in quantity in different breeds. . . . . Where there is a deficiency of yolk, the fibre of the wool is dry, and harsh, and weak, and the whole fleece becomes hairy; while where the quantity of yolk is abundant, the wool is soft, and oily, and plentiful, and strong.' Dr. Ure says: 'Formerly it was considered as a kind of soap, mainly for the reason that the wool besides this sometimes contained about 8 p.c. of fat. This fat, however, is usually combined with earthy matters, mostly with lime, and consequently forms a soap which is very insoluble. The soluble suint is a natural salt (sudorate of potash) arising from the combination of potash with a peculiar animal acid, of which little is known.' *V.* Wool grease.

When the suint is removed by washing, a solid and a more liquid fat may be extracted by alcohol. These two fats may be separated owing to their different solubility in alcohol. They were examined by Chevreul, who named the solid *stearerin* and the liquid *elairerin*. For a complete examination of wool, see The Structure of the Wool Fibre, by F. H. Bowman, D.Sc.

WOOL, BLACK, *v.* Azo- colouring matters.

WOOL GREASE. The exudations of sheep, which collect on their wool, are well known to contain substances soluble in water, and substances insoluble in water, but soluble in alkalis. Buisine finds that the substances soluble in pure water contain numerous potassium compounds. He observed the presence of (1) free carbonic acid; (2) ammonium carbonate (by the decomposition of urea); (3) potassium carbonate (due to a peculiar fermentation which goes on at the cost of certain secreted substances; (4) volatile fatty acids — viz. acetic, propionic, butyric, valeric, and capronic acids; (5) higher fatty acids, such as œnanthic, caprinic, oleic, stearic acids, and particularly cerotinic acid. These are present as potassium salts, which are formed on the skin or by washing in consequence of saponification by potassium carbonate; (6) fat in the state of an emulsion; (7) phenol as potassium sulphonate; (8) lactic acid; (9) benzoic acid; (10) oxalic acid; (11) succinic acid; (12) uric acid; (13) amido- acids—viz., glycocol, leucin, tyrosin; (14) colouring matter, the same as in the urine. The aqueous extract of the wool consequently contains all substances (or their decomposition products) generally found in the urine of herbivorous animals. The extracts may become a valuable source for obtaining acetic, propionic, benzoic, lactic, and caprinic acids, these being present in considerable quantities. The grease of an Australian wool gave in 100 parts dry residue : 7·1 parts acetic acid, 4 parts propionic acid, 2·6 parts benzoic acid, and 1 part caprinic acid (A. Buisine, C. R. 103, 66; S. C. I. 5, 539) *v.* Oleic acids.

WOOL SCARLET *v.* Azo- colouring matters.

WOOTZ. An Indian name for steel.

WORMSEED *v.* Santonica.

WORMSEED, OIL OF, *v.* Oils, essential.

WORMWOOD. The leaves and tops of *Artemisia, Absinthium* contain a volatile oil, *Absinthol* (*q.v.*) and a bitter principle, *Absinthin* (*q. v.*). Wormwood is a bitter stomachic tonic, and is used in medicine as a remedy for atonic dyspepsia, and as an anthelmintic.

WOURALI, WOURARA, WOURARI *v.* Curara.

WULFENITE *v.* Molybdenum.

X

XANTHEIN. The name applied by Fremy and Cloez to the soluble yellow colouring matter of flowers.

XANTHIC ACID (*Ethyl-oxydithio-carbonic acid*) $CS.SH.OC_2H_5$. The potassium salt of this acid is readily obtained by the action of carbon bisulphide on an alcoholic solution of potash, and from this salt the acid may be prepared by treatment with dilute sulphuric or hydrochloric acid; is a heavy, colourless oil of a penetrating smell and taste. It is readily decomposed on warming into carbon bisulphide and alcohol. The soda salt has acquired some industrial importance on account of its application in printing with artificial indigo, and as a remedy against phylloxera, *v.* vol. ii. p. 390.

XANTHINE $C_5H_4N_4O_2$. A white, granular, microcrystalline powder, constituting a rare form of urinary calculus; found in urine; is a normal constituent of the animal body, present in muscular fibre, in the liver, pancreas, spleen, and brain. Found in guano and in yeast. Forms salts with sulphuric and hydrochloric acids.

XANTHOGALLOL *v.* Phenol and its homologues.

XANTHORRHAMNIN *v.* Persian Berries.

XANTHORRHŒA RESINS or **BALSAMS** *v.* Balsams.

XANTHOXYLUM. The bark of the prickly ash, *X. fraxineum* and *X. carolinianum.* Is used in medicine in the treatment of rheumatism and to relieve toothache. It contains a volatile oil and resin.

XYLENES, *Dimethylbenzenes,*

$$C_8H_{10} = C_6H_4(CH_3)_2.$$

A hydrocarbon of the formula C_8H_{10} (in reality a mixture) was obtained by various investigators from the fraction of coal-tar, or of wood-tar, boiling about 140°. De la Rue and H. Müller isolated a similar substance from Rangoon tar. Fittig (A. 153, 265) showed that the crude xylene from coal tar contained two isomeric hydrocarbons—*metaxylene*, which he had previously obtained by distilling mesitylenic acid

$$C_6H_3(COOH)(CH_3)_2(1{:}3{:}5)$$

with lime; and *paraxylene*, which he had prepared by the action of sodium on a mixture of crude bromtoluene and methyl iodide; but pure paraxylene was first prepared by Jannasch (A. 156, 239), by employing pure parabromtoluene in the same reaction. *Orthoxylene* was first isolated from coal-tar by Jacobsen (B. 10, 1,010), but had previously been obtained by Fittig and Bieber (A. 171, 79) by the distillation of paraxylic acid $C_6H_3(COOH)(CH_3)_2(1{:}3{:}4)$ with lime.

Crude coal-tar xylene, containing paraffins and other hydrocarbons, was formerly used only as solvent naphtha. At present, purified xylene is employed in the manufacture of xylidine scarlet and other azo- colours.

The xylenes are formed, like other methyl homologues of benzene, by the decomposition of complex organic substances by heat, hence their occurrence in coal-tar and wood-tar. The meta-compound is formed in the largest quantity; but the relative proportion of the three isomerides varies both with the material distilled and with the temperature at which the distillation is conducted. The separation of the three xylenes is a somewhat complex process (*v. infra*). In like manner xylenes are formed, together with other hydrocarbons, when the vapour of oil of turpentine is passed through a red-hot tube. Ortho-xylene, with about 5 p.c. of para-xylene, is formed when methyl chloride is passed into warm toluene containing aluminium chloride. The xylenes are also formed by the distillation of the dimethylbenzoic acids with lime.

In order to separate the isomerides, a commercial xylene, boiling at about 140°, and freed from phenols and bases by treatment with alkali and acid, is employed as the starting-point. If only the meta- compound, which alone is of technical importance, is required, the mixture is boiled with dilute nitric acid (1 part of commercial acid of sp.gr. 1·4 with 2 parts of water); the ortho- and para- compounds are thus converted into acids, whilst the meta- compound is hardly attacked (Fittig and Velguth, A. 148, 10). The product is steam-distilled, the distillate shaken with alkali to free it from acids and nitro-xylenols, dried, and rectified.

O. Jacobsen (B. 10, 1013; 11, 17) has described a method by which the three isomerides may be isolated from coal-tar xylene. The crude xylene is shaken in the cold with concentrated sulphuric acid, which dissolves ortho- and meta-xylene, converting them into sulphonic acids, whereas para-xylene is hardly attacked, even on heating. In order to obtain the ortho- and meta-xylene, the acid solution is treated with excess of calcium carbonate, filtered from calcium sulphate, the filtrate, containing the calcium sulphonates, precipitated with sodium carbonate, and the solution of the sodium xylene-sulphonates concentrated by evaporation and allowed to crystallise. Sodium ortho-xylene-sulphonate separates, whilst the sodium salts of two isomeric meta-xylene-sulphonic acids remain in solution. In order to purify the para-xylene, it is gently warmed with fuming sulphuric acid, in which it dissolves, leaving behind a paraffin and other impurities. The three xylenes are then liberated from their sulphonic acids by hydrolysis with concentrated hydrochloric acid at 195°.

The hydrocarbons may, of course, also be regenerated from the sulphonic acids by the dry distillation of the ammonium salts alone, or of the other salts with dry ammonium chloride.

Armstrong and Miller (C. J. 1884, 151, footnote) point out, with reference to Jacobsen's method of separation, that para-xylene dissolves in concentrated sulphuric acid almost as readily as meta-xylene. Levinstein, however (S. C. I. 1884, 354), shows that this only applies to pure para-xylene, and that, when the para-xylene is mixed with paraffins and the other substances present in coal-tar xylene, it is, as stated by Jacobsen, only very slightly soluble in sulphuric acid.

Noelting and Palmar (B. 24, 1955) have shown that commercial xylene contains ethylbenzene, and that in Jacobsen's method of separating the isomers the para-xylene is obtained mixed with this hydrocarbon.

PROPERTIES.

Ortho-xylene, $C_6H_4(CH_3)_2$,(1:2). Liquid, boiling at 144° (cor.). Oxidised by dilute nitric acid to orthotoluic acid, $C_6H_4(CH_3)(COOH)$,(1:2), melting at 102°. A hot solution of potassium permanganate oxidises it to orthotoluic and phthalic acids, whilst chromic acid totally destroys it. Concentrated sulphuric acid converts it into a sulphonic acid, of which the chloride melts at 52°, and the amide at 144°.

Meta-xylene (Iso-xylene), $C_6H_4(CH_3)_2$,(1:3). Liquid, boiling at 139° (cor.). Sp.gr. 0·8715 at $\frac{12·3°}{4°}$. Not attacked by dilute nitric acid. Chromic acid oxidises it to isophthalic acid. When warmed with concentrated nitric acid it yields a tri-nitro- derivative, $C_6H(CH_3)_2(NO_2)_3$, melting at 176°, very sparingly soluble in alcohol. Concentrated sulphuric acid converts it into a mixture of two sulphonic acids.

Para-xylene, $C_6H_4(CH_3)_2$,(1:4). Monoclinic prisms. Melts at 15°, and boils at 138·2°. Sp.gr. 0·8621 at 19·5°. Dilute nitric acid oxidises it to paratoluic acid, $C_6H_4(CH_3)(COOH)$,(1,4), melting at 178°; chromic acid to terephthalic acid. Sulphuric acid converts it into a sulphonic acid, of which the chloride melts at 26°, and the amide at 148°.

Commercial xylene should have been previously washed with sulphuric acid, and should, therefore, give only a pale-brown colouration on treatment with concentrated sulphuric acid. The boiling-point of the product should lie within a few degrees; thus not more than 10 p.c. should distil below 138°, and not more than 10 p.c. above 140·5°, the remainder passing over between these two temperatures.

The xylene of commerce is a product of very variable composition. The relative proportion of the three isomerides varies in different samples, and as these three compounds have almost identical boiling-points, the boiling-point of such a mixture affords no clue to its composition. The value of a commercial xylene depends on the quantity of meta-xylene which it contains. Methods for the quantitative estimation of the three xylenes in the commercial product have been devised (*v.* Levinstein, S. C. I. 1884, 77; Reuter, B. 1884, 2028, and S. C. I. 1884, 626; Chem. Zeit. 13, 830; and S. C. I. 1889, 874). F. R. J.

XYLENOLS *v.* PHENOL AND ITS HOMOLOGUES.

XYLIDINE (*Amidoxylene, Amidodimethylbenzene*). Theory predicts the existence of six isomeric amidodimethylbenzenes, all of which are known. They are obtained by the reduction of the corresponding nitro- compounds with tin and hydrochloric acid, or with iron filings and acetic acid, or, in the case of the commercial product, with iron turnings and hydrochloric acid.

1. **ν-Orthoxylidine**,

$C_6H_3(CH_3)_2NH_2,(CH_3{:}CH_3{:}NH_2 = 1{:}2{:}3)$.

Liquid, boiling at 223° (cor.). Sp.gr. 0·991 at 15°. Melting-point of the acetyl compound, $C_6H_3(CH_3)_2NH(C_2H_3O)$, 131°.

2. **α-Orthoxylidine**,

$C_6H_3(CH_3)_2NH_2,(CH_3{:}CH_3{:}NH_2 = 1{:}2{:}4)$.

Lustrous rhomboidal tables, or large monoclinic crystals, melting at 49°. B.p. 226°. M.p. of acetyl compound 99°.

3. *v*-**Metaxylidine**,
$C_6H_3(CH_3)_2NH_2,(CH_3:NH_2:CH_3 = 1:2:3)$.
Liquid, boiling at 216° (cor.). M.p. of acetyl compound 174 .

4. *a*-**Metaxylidine**,
$C_6H_3(CH_3)_2NH_2,(CH_3:CH_3:NH_2 = 1:3:4)$.
Liquid, boiling at 212°. Sp.gr. 0·9184 at 15°. M.p. of acetyl compound 129°.

5. *s*-**Metaxylidine**,
$C_6H_3(CH_3)_2NH_2,(CH_3:CH_3:NH_2 = 1:3:5)$.
Liquid, boiling at 220–221° (cor.). Sp.gr. 0·9935 at 0°. M.p. of acetyl compound 140·5°.

6. **Paraxylidine**,
$C_6H_3(CH_3)_2NH_2,(CH_3:NH_2:CH_3 = 1:2:4)$.
Liquid, boiling at 220–221°. Sp.gr. 0·980 at 15°. M.p. of acetyl compound 138–139°.

COMMERCIAL XYLIDINE.

The nitroxylene used in the manufacture of this product is prepared by the action of nitric acid on coal-tar xylene—a mixture of three isomeric xylenes together with a small quantity of ethylbenzene (*v.* XYLENE). As ortho-xylene yields by direct nitration two mononitro-xylenes, meta-xylene two, and para-xylene one, it is evident that these five nitro-xylenes will be contained in commercial nitro-xylene, and, therefore, that the five corresponding xylidines will be present in the commercial xylidine obtained from it by reduction with iron turnings and hydrochloric acid. *a*-Meta-xylidine is present in largest quantity; next to it, para-xylidine is the chief constituent, occurring to the extent of 20–25 p.c. If commercial xylidine is mixed with excess of concentrated hydrochloric acid, a magma of crystals separates, consisting mainly of the hydrochloride of *a*-metaxylidine (Schultz, Steinkohlentheer, 1, 339). Paraxylidine may be separated by the greater solubility of its sulphonic acid in dilute sulphuric acid, the base being afterwards regenerated by distilling the sodium salt of the sulphonic acid with dry ammonium chloride (Witt, Noelting, and Forel, S. C. I. 1889, 274). Commercial xylidine also contains amido-ethylbenzene (Noelting and Palmar, B. 24, 1,957).

For the preparation of colouring matters, Limpach (Eng. Pat. 6,899, May 9, 1888; S. C. I. 1889, 281) proposes to separate the xylidines from the commercial product by the following method: 121 grms. of commercial xylidine are treated with 30 grms. of 100 p.c. acetic acid, and allowed to stand for twenty-four hours. Crystals separate out, which consist of pure *a*-metaxylidine acetate. The mother-liquors are treated with hydrochloric acid, and after standing three to four days, about 20–25 p.c. of para-xylidine separates as hydrochloride. The filtrate from this contains principally derivatives of orthoxylidine.

Commercial xylidine is employed exclusively in the preparation of azo- colours, for which purpose it is either converted direct into diazoxylene, or first into amido-azo-xylene or into cumidine.

It should distil for the most part between the temperatures of 212° and 218°. F. R. J.

XYLIDINE PONCEAU *v.* AZO- COLOURING MATTERS.

XYLIDINE RED *v.* AZO- COLOURING MATTERS.

XYLIDINE SCARLET *v.* AZO- COLOURING MATTERS.

XYLITE *v.* WOOD, DISTILLATION OF.

XYLONITE *v.* CELLULOID.

XYLORETIN *v.* RESINS.

XYLOÏDIN. A name applied by Braconnot to an explosive product, $C_6H_8(NO_2)O_5$, obtained by the action of nitric acid on starch; and also to some varieties of collodion prepared by the action of nitric acid on wood-cellulose.

XYLOSE $C_5H_{10}O_5$, a penta-glycose discovered by Koch (B. 20, 145), and obtained by the hydrolysis of *wood-gum* extracted from wood by dilute soda solution. Xylose crystallises in brilliant white needles; m.p. 144–145°; dextrorotatory, +18° to 19°. Shows the phenomenon of bi-rotation very strongly. Like arabinose, it gives no levulinic acid on boiling with hydrochloric acid, nor mucic or saccharic acid on treatment with nitric acid. Yields furfuramide on heating with sulphuric acid. Gives a cherry-red colour with hydrochloric acid and phloroglucin. With phenylhydrazine forms long, silky, yellow needles, $C_{17}H_{20}N_4O_3$. On oxidation with nitric acid, yields trihydroxyglutaric and trihydroxybutyric acids (Wheeler and Tollens, A. 254, 304).

According to Bertrand (Bl. [3] 5, 554), xylose may be obtained from wheat- or oat-straw by first extracting the straw with tepid water, and then boiling it for several hours with dilute (1 to 2 p.c.) sulphuric acid. The liquor, after removal of the sulphuric acid by baryta, is concentrated on the water-bath and treated with alcohol; this extracts the xylose, which forms a syrup on evaporation of the alcohol, solidifying on the addition of a crystal of xylose. The yield is about 2 p.c. from wheat-straw, and 4 p.c. from oat-straw.

Xylose appears to be the aldehyde of an open-chain alcohol *xylitol* (Bl. [3] 5, 740).

Y

YEAST *v.* FERMENTATION.

YELLOW, ACID, *v.* AZO- COLOURING MATTERS; also NAPHTHALENE.

YELLOW, ANILINE, *v.* AZO- COLOURING MATTERS.

YELLOW, BRILLIANT, *v.* AZO- COLOURING MATTERS; also NAPHTHALENE.

YELLOW, BUTTER, *v.* AZO- COLOURING MATTERS.

YELLOW, CAMPOBELLO, *v.* NAPHTHALENE.

YELLOW, CHROME, *v.* CHROMIUM.

YELLOW, CITRON, *v.* CHROMIUM.

YELLOW, COLOGNE, *v.* CHROMIUM.

YELLOW, CONGO, *v.* AZO- COLOURING MATTERS.

YELLOW COPPER ORE *v.* Copper.

YELLOW, CROCEÏN, *v.* Naphthalene.

YELLOW, DIPHENYLAMINE, *v.* Azo-colouring matters.

YELLOW, FAST, *v.* Azo- colouring matters.

YELLOW, FRENCH, *v.* Azo- colouring matters.

YELLOW, HESSIAN, *v.* Azo- colouring matters.

YELLOW, IMPERIAL, *v.* Aurantia.

YELLOW, GOLDEN, *v.* Naphthalene.

YELLOW, KING'S, *v.* Arsenic; also Pigments.

YELLOW, LEIPSIC, *v.* Chromium.

YELLOW, LEMON, *v.* Chromium.

YELLOW, MANCHESTER, *v.* Naphthalene.

YELLOW, MARTIUS'S. *v.* Naphthalene.

YELLOW METAL, *v.* Copper.

YELLOW, METANIL, *v.* Azo- colouring matters.

YELLOW, NAPHTHALENE, *v.* Naphthalene.

YELLOW, NAPHTHOL, *v.* Naphthalene.

YELLOW, NEW, *v.* Naphthalene.

YELLOW, ORANGE, *v.* Azo- colouring matters.

YELLOW, PARIS. *Lead chromate v.* Chromium.

YELLOW PASTE *v.* Azo- colouring matters.

YELLOW, RESORCIN, *v.* Azo- colouring matters.

YELLOW, TURNER'S, *v.* Lead.

YELLOW ULTRAMARINE. *Citron yellow, Lemon yellow. Barium chromate v.* Chromium; also Pigments.

YELLOW, SAFFRON, *v.* Naphthalene.

YELLOW, SALICYLIC, *v.* Salicylic yellow.

YELLOW, SUN, *v.* Azo- colouring matters; also Stilbene.

YELLOW WOOD *v.* Fustic.

YEW. *Taxus*; *If commun*, Fr.; *Eibe*, Ger. It has long been known that the leaves and berries of the common yew, *Taxus baccata* (Linn.), (Bentl. a. T. 253), possess powerful toxic properties. Yew is a reputed emmenagogue, and it has been used for the purpose of procuring criminal abortion, but its efficiency is more than doubtful, and its employment often leads to fatal consequences (*cf.* Redwood, Ph. [3] 8, 361). The first thing to do in cases of poisoning is to empty the stomach; milk may then be given to allay irritation, and such stimulants as alcohol or ammonia employed. Yew is seldom used in medicine.

Chevallier a. Lassaigne (J. Ph. 1818, 4, 558), Peretti (J. Ph. 1828, 14, 537), Lucas (Ar. Ph. [2] 85, 145), and others have examined yew chemically, but no definite compound was isolated till the discovery of an alkaloid *taxine* by Marmé in 1876 (C. C. 1876, 166). Taxine was further studied by Amato a. Capparelli (G. 10, 349), who also obtained a non-nitrogenous crystalline compound *milossin*, and a *volatile oil* which distils with steam, and has the odour of fennel. The chemical reactions of taxine obtained by Marmé's process have been examined by Hilgar and Brande (B. 23, 464). Taxine is prepared by exhausting yew leaves or seeds with ether. The residue, after distilling off the ether, is extracted with acidulated water, and from the clear aqueous solution alkalis precipitate the base in white flakes, which, when washed and dried over sulphuric acid, assume the appearance of a white crystalline powder. The leaves contain more alkaloid than the seeds. Taxine melts at 80°. It is odourless, but possesses a very bitter taste. It is very slightly soluble in water, is soluble in dilute acids, alcohol, ether, benzene, and chloroform, and insoluble in petroleum ether. Sulphuric acid reddens it. No precipitate is formed on the addition of platinic or auric chloride, but amorphous precipitates are obtained with most of the other alkaloidal reagents (Marmé). From the residue, insoluble in acidulated water, alcohol and animal charcoal extracts milossin. Its purification is tedious and difficult. It crystallises in stellate groups of needles, which melt at 86–87°, and which are insoluble in water, but soluble in boiling alcohol (Am. a. C.).

According to Hilger and Brande, taxine (m.p. 82°) is a monovalent base, having the formula $C_{37}H_{52}O_{10}N$. The following compounds were prepared and analysed:

Hydrochloride, $C_{37}H_{52}O_{10}N,HCl$;
Sulphate, $(C_{37}H_{52}O_{10}N)_2H_2SO_4$;
Platinum salt, $(C_{37}H_{52}O_{10}NHCl)_2PtCl_4$;
Gold salt, $C_{37}H_{52}O_{10}NHCl,AuCl_3$;
and Ethoiodide, $C_{37}H_{52}O_{10}N,C_2H_5I$.

A. S.

YTTRIUM *v.* Cerium metals.

YTTERBIUM *v.* Cerium metals.

Z

ZAFFRE. *Cobalt blue v.* Cobalt, also Pigment.

ZALA. A synonym for Borax.

ZEIODELITE. The name of a mixture obtained by stirring 24 parts of finely powdered glass into 20 parts of melted sulphur, and used as a cement and for taking casts instead of sulphur or plaster.

ZINC. Symbol Zn. At.wt. 64·88.

Zinc was discovered last of the seven common metals, it being first mentioned as a metal by Paracelsus about 1530. But ores of zinc were known to the ancients, and were employed by them both for the manufacture of brass by the calamine process, and also in medicine. The working of zinc ores in Europe in modern times dates from the introduction of the use of brass, and there are records extant which show that in 1439 the Vieille Montagne calamine mines had been worked for a considerable time by the men of Aix. Metallic zinc was sometimes produced accidentally during the smelting of copper, but is stated to have been first made directly from calamine by Henckel in 1721 (Percy, Metallurgy, 1, p. 520). A zinc factory was erected at Bristol shortly afterwards; but the production in this country was small, the greater part of the metal which was required being imported from China and India, and zinc is stated to have sold in 1731 for 260*l.* per ton, or more than ten times its present value. Other works were erected in the United Kingdom, and the demand gradually increased with the introduction of the direct method for the manufacture of brass. In England the process of distillation *per descensum* in fireclay crucibles was adopted; this has scarcely been used elsewhere, and is now completely abandoned in this country. The Liège (or Belgian) process was invented by Daniel Douy in 1809, and works were immediately erected for carrying out the process at Liège. These works ultimately developed into the Société de la Vieille Montagne, in 1837, and this Société is now the largest zinc-producing company in the world. Zinc has also been manufactured on a considerable scale for a lengthened period in Germany, particularly in Silesia. It was not till 1820 that the exports of zinc from England to India about equalled the total imports, and this country could be considered for the first time to supply itself with zinc. Since that time, however, the trade has fluctuated considerably, so that in 1864 the total production of zinc in the United Kingdom did not equal one half of that required in the Birmingham brass trade alone. The following figures, taken from a paper by M. Paul de Sinçay, 'On the Manufacture of Zinc in Belgium' (Inst. M. E. 1883, 345), give the approximate production, in Belgian tonnes, of raw zinc in Europe:—

—	1860	1870	1880
Upper Silesia	40,354	36,518	65,437
Vieille Montagne	28,925	42,112	44,690
Other Belgian makers	9,144	14,476	26,700
Rhenish Provinces and Westphalia	8,592	18,006	27,107
England	6,104	16,000	22,000
Other countries	4,777	8,173	23,253
Total	97,896	135,285	209,187

The European production of zinc in 1888 was as follows:

Upper Silesia	83,375 tons
Belgium and Rhenish Provinces	133,245 ,,
Great Britain	26,633 ,,
Other countries	23,752 ,,
Total	267,005 ,,

The production of the United States of America, which in 1880 amounted only to 20,749 metric tons, had risen in 1888 to 57,000 metric tons. Of this quantity 10,400 tons was produced in the Eastern and Southern States, 22,500 tons in Illinois, and the remaining 24,100 tons in Kansas and Missouri (J. Soc. Chem. Indust. 8, pp. 483, 151).

Ores of zinc. The most important ores of zinc are the sulphide and carbonate. *Zinc blende* (ZnS) is commonly called 'black jack' by the miner on account of its dead black colour and high lustre. The use of blende for the manufacture of zinc and brass was patented in 1758 by Champion, of Bristol. Previously the source of the metal was the carbonate *calamine* ($ZnCO_3$) and this was the only ore used in Belgium until about 1855, when roasting of blende was adopted. Both these ores are widely distributed and are now extensively employed. Of less importance are the oxide (which usually contains oxides of manganese, and from its colour is called red oxide of zinc) and the silicates.

In New Jersey red oxide of zinc occurs together with magnetic oxide of iron in *Franklinite* from which the zinc is first extracted, and the residue is afterwards smelted for spiegel-eisen in the blast furnace. The flue dust from the blast furnace used in the manufacture of iron is also frequently sufficiently rich in zinc to render its extraction advantageous. The total quantity of zinc ore raised in the United Kingdom in 1887 was 25,445 tons, containing on the average 51 p.c. of zinc and valued at 76,182*l.*, the chief sources being North Wales, the Isle of Man, and Cumberland. The Derbyshire mines, once of great importance, only yielded 2 tons of zinc ore in 1887. In addition to the above, 17,738 tons of zinc ore were imported, valued at 71,301*l.*

Extraction of zinc. It is necessary that the ores used for the extraction of zinc should be as rich and as uniform in character as possible. The ores as they occur are often only poor in zinc, and require to be concentrated by washing; in the case of calamine ores this is usually a tolerably simple matter, but with blendes which are frequently associated with other sulphides concentration is a more complicated operation, though with modern appliances, careful sizing, and the necessary attention, a remarkably perfect separation can be effected. The slimes produced during concentration are again treated, 'frue vanners' being now used for this purpose at Freiberg, and such portions as are rich in zinc are dried and smelted in mixture with other materials as afterwards described. When the ores have been thus concentrated, they are calcined or roasted to convert them as completely as possible into zinc oxide. Calamine is readily calcined, and this is frequently conducted in kilns with the waste heat from the smelting furnaces. On the other hand, blende requires much care and experience in roasting, so as to prevent the formation of difficultly decomposable sulphate. Blende is generally roasted in double-bedded reverberatory furnaces, frequently with the waste heat from the smelting furnaces. By the use of double-bedded roasting furnaces a considerable economy of fuel, and more uniform heating is obtained. It has generally been considered that the presence of any sulphur in roasted blende leads to loss of zinc, owing to sulphide being left in the retort, but, according to A. Voigt (J. S. C. I. 8, 986), the zinc left in the retort is chiefly in the form of oxide, while the sulphur in roasted blende is in the form of sulphates of metals generally other than zinc, and the presence of a small quantity of sulphur in roasted blende does not reduce the yield of zinc. The time required for roasting different varieties of blende varies from about two to six hours, and is longest with ores rich in iron pyrites.

In roasting blendes a quantity of zinc fume is produced, and may lead to a somewhat considerable loss of zinc. This fume has been utilised by Dr. Krause-Cöthen for the manufacture of zinc carbonate (Berg. u. Hütt. Zeit. 1891, 246). The blende roasted at Oberhausen contains 0·02 p.c. of mercury. The dust deposited from the roasting kilns contains about 7 p.c. of mercury, which is extracted, and the sulphur dioxide from the gases is used for the manufacture of anhydrous sulphurous acid (Chem. Zeit. 10, 1039).

After calcination the finely divided ore is in all cases mixed with a suitable proportion of ground coal (non-caking) or other carbonaceous material, and heated to bright redness in a retort, the form and dimensions of which vary with the locality and the nature of the ore. The carbon unites with the oxygen of the ore to form carbonic oxide, and zinc is set free; the metal at the high temperature employed is converted into vapour, which is caused to pass into suitable receptacles, and condensed. The processes which are or have been used for the extraction of zinc differ merely in the form, arrangement, and number of the retorts, and in the methods adopted for supporting and heating them.

It is advantageous to thoroughly crush the materials, and to have as large a condensing space as possible. The condensers should be just sufficiently hot to keep the condensed metal in the liquid state, as, if the receivers are too hot, zinc is lost by volatilisation, while if the temperature is too low a coarse crystalline product is obtained. It is necessary that the retorts should be kept filled with carbonic oxide; if carbon dioxide is present, part of the zinc is oxidised and zinc and zinc oxide distil over together. For this reason it is necessary to leave a little of the ore unreduced in the retort at the end of the process (Steger, S. C. I. 5, 607).

The following general principles have been laid down for the construction of zinc furnaces by M. F. Laur (Bull. Soc. Indust. Minérale, 1874, 3, 395; Inst. C. E. 41, 317):

1. That it is not prudent to construct furnaces the internal capacity of which exceeds about 32·5 cubic yards.

2. The thickness of the charge to be reduced in the muffles should not exceed 7 inches, and the vessels should not exceed 20 inches in height, or 5 feet in length.

3. The maximum capacity which can be advantageously given to the retorts is about twenty-two gallons.

4. The total interior volume of the retorts should be about one-third of the volume of the furnace in which they are heated, since experience shows that about two-thirds of the space is required for supports and free circulation.

Four processes for the extraction of zinc have been actually worked on a considerable scale—namely, the English, Carinthian, Belgian, and Silesian.

1. In the *English process*, adopted by Champion at Bristol, large fire-clay crucibles were used, and the method was that known as distillation *per descensum*. The process involved the use of an excessive amount of fuel, and only a comparatively small amount of zinc could be produced. This manufacture forms a very interesting chapter in the metallurgy of zinc, and has been fully treated by Dr. Percy (Metallurgy, 1, 550), but as it has been entirely superseded, will not be here described in detail.

2. *The Carinthian process.* The process formerly adopted in Carinthia was in principle similar to the English method, the ore being charged into vertical pipes or retorts of fire-clay, and distillation being effected *per descensum*; a single furnace sometimes contained over 250 such pipes. This process is also now abandoned.

3 and 4. *Belgian and Silesian processes.* The only processes now in extensive operation are the Belgian and Silesian, neither of which are confined to the countries in which they were invented, and the two systems are sometimes combined in the same furnace, the retorts in the lower or hotter part being on the Silesian principle, and in the upper part on the Belgian. In each case the retorts are of fire-clay, and are generally made on the premises, being carefully moulded by hand, then air-dried for about a fortnight, and afterwards heated to redness in a separate furnace before being set in position. By an improvement, the invention of M. Dor, which has been largely adopted in Belgium, the retorts are subjected to a pressure of 3,000 lbs. to the square inch during manufacture; they are afterwards bored by machinery, and are thus made very thin, and yet possess great durability. The differences between the Belgian and Silesian systems are in the shape, size, and method of supporting the retorts, in the amount of charge used, and in the arrangement of the retorts in the furnace. In each system direct firing by coal was formerly universal and is still occasionally used, but gas-firing is now very generally adopted, and the use of the Siemens' and other gas furnaces is found to be most advantageous. The introduction of gas furnaces has led to considerable saving of fuel, which in Silesia was formerly 3·5 tons of coal per ton of ore, and is now about one-third of that quantity; gas firing has also led to the use of larger furnaces and given longer life to the retorts. The result has been that, in Silesia, while in recent years the number of works has actually decreased, the production of zinc has greatly increased (*v.* M. Georgi, Zinc Industry of Upper Silesia; Berg. u. Hütt. Zeitung, 36, 71, 78, 97; Inst. C. E. 49, 369).

The retorts used in the *Belgian process* are cylindrical or elliptical in shape, being closed at one end; these retorts are supported at the extremities, and are set in the furnace in tiers, each retort being inclined, and higher at the back than the front. The elliptical retorts are used for the lower tiers, where the temperature is highest, and they are sometimes air-cooled at the bottom. When the charge has been introduced, which requires considerable skill, the mouths of the retorts are fitted with condensing tubes of clay in which the zinc collects, partly in the form of metal and partly in the form of more or less oxidised dust, which deposits chiefly in a sheet-iron nozzle which is fitted to the clay tube. The workman judges of the progress of the operation by the colour of the flame or vapours which are evolved. Brown vapours are first given off, and with these any cadmium passes over; they are succeeded by the characteristic flame of zinc, which continues until the operation is completed. The loss of zinc by the Belgian process is about 15 to 20 p.c. of that originally present in the ore; while in the Silesian process, in which poorer and more refractory ores are employed, the loss is 5, or even 10, p.c. greater.

In the *Silesian process* the retorts are ⌓ shaped; the width is the same as that of the Belgian retorts, but the height is greater, and as the retorts are supported in the furnace from beneath, they are made longer than in the Belgian process—consequently the charge is greater. The retorts are usually placed in a single row in the furnace, which occasionally contains as many as forty such retorts, though about thirty-two is stated to give the best results, and a smaller number is frequently employed. In the latest form of Silesian furnace at Freiberg the muffles are arranged in two rows one above the other, and each row contains sixteen muffles. In recent years the tendency has been to use a much larger number of retorts than formerly, so that the charge of ore per furnace has been raised from 15 cwt. to 6 or 8 tons.

In the lower part of the front of a Silesian muffle a hole is provided for the purpose of introducing the charge, and removing the residue after the distillation is complete. This method of charging, combined with the underneath support, gives greater durability to the Silesian muffles, so that, though in a given time the Belgian furnace may make more zinc, the annual production is rather in favour of Silesia (*v.* F. A. Thum, Notes on Zinc Smelting, Eng. and Min. Jour. 1879, 275; Inst. C. E. 58, 407).

The zinc works of Prince Hohenlohe in Silesia include three smelting works, with a total of 106 furnaces, and a separate calcining works for the preparation of zinc blende for distillation. The fourteen long double-bedded calcining furnaces employed have each an output of 220 lbs. of roasted ore every five hours. Each zinc furnace contains thirty-two muffles, heated by gas from Boetius producers. Every furnace is arranged with sixteen niches, each containing two muffles, while two furnaces are built together so as to form a double furnace. Two spaces are provided at either end of the double furnace, one for tempering the muffles, and the other for calcining the lump calamine. Most of the calamine is charged raw, as the carbon dioxide is driven off long before the temperature of reduction is reached. The charge per muffle weighs 507 lbs., and consists of a mixture of roasted blende, lump calamine, and dried slimes. The daily yield is about 108 lbs. of zinc. The zinc contains 3 to 4 p.c. of lead, which is reduced by refining to 1·07 p.c. The refining is conducted in a reverberatory furnace with an inclined base, in the well of which the metal collects, the lead at the bottom and the zinc above. Every twelve hours about half a ton of zinc is tapped, and the same amount of raw zinc is charged in; the lead is removed at longer intervals. An exactly similar process is used in Birmingham for refining Continental zinc previous to rolling. The refined zinc contains about 1 p c. of lead, 0·02 p.c. of iron, and 0·04 p.c. of sulphur (Berg. und Hütt. J. 1889, p. 389; Inst. C. E. 101, 382).

According to L. Grand, the zinc ores smelted at Freiberg are blendes which contain about 35 p.c. of zinc, 30 p.c. of sulphur, and 4 to 5 p.c. of lead. The ores also contain iron and arsenic. They are first roasted in kilns to utilise the sulphur, and then roasted more completely in double-bedded calciners until they contain not above 1 p.c. of sulphur. Distillation is effected in Silesian furnaces, each of which is heated by gas on the Siemens' regenerative principle, and contains thirty-two muffles. The charge of each muffle is 100 lbs. of calcined blende, which requires twenty-four hours for distillation, and yields about 32 lbs. of zinc. Such a charge requires for fuel 50 lbs. weight of coal and 5 to 6 cubic feet of wood. The muffles last about six weeks (Ann. M. [2] 1875, 261; Inst. C. E. 42, 345).

Treatment of zinc ores in the blast furnace. In order to reduce the consumption of fuel and labour in the extraction of zinc a number of attempts have been made to reduce zinc in the blast furnace, but hitherto without much success. The difficulty experienced is due to the fact that the vapour of zinc and the furnace gases must, in such a furnace, pass away together, and during the condensation which ensues a reaction takes place between the zinc and the carbon dioxide of the gases, thus $Zn + CO_2 = ZnO + CO$ reproducing oxide of zinc, and the ultimate result of the operation is merely to carry oxide of zinc out of the blast furnace into the condensing apparatus. This action has been studied by Lencauchez (Mém. Soc. Ingén. Civils, 1877, 568; Inst. C. E. 51, 332), who found that zinc was still oxidised when the proportion of carbon dioxide was only 0·5 p.c. of the gas employed. By very rapid cooling of the gases Lencauchez succeeded in reducing the oxidation of the zinc to as little as 5 p.c., but after numerous experiments he concluded that this process is not likely to be commercially successful.

In 1878 Binon and Grandfils, in Stolberg, made the attempt to use a zinc oven with upright retorts. They aimed at making the old Carinthian method continuous. The materials containing zinc were heated with reducing agents by gas in reduction spaces in the form of shafts, which were filled above and emptied below.

The zinc shaft furnaces of Henri Harmet have above and below an apparatus for leading off the zinc vapours. The volatile products are led through two long cylindrical upright chambers, filled with incandescent fuel, in which the reduction of carbonic acid to carbonic oxide and traces of zinc oxide to metallic zinc is completed. Westman, in the year 1884–5, used two shaft furnaces, supplied with coal, and one for preparing briquettes of ore and coal. Through both the first shaft furnaces generator gas was passed, by the combustion of which in the regenerating chambers sufficient heat was produced to reduce the ore to metal. This has been further improved by Westman in Eng. Pat. 17336, 1888. Quaglio, Pintich, and Lentz obtained a patent in 1884 for a furnace construction, which consists in the arrangement of two shaft ovens connected by a canal, into one of which the air is introduced, and from the other the products of the reaction are withdrawn, this constantly being reversed. The patentees indicate that the principle of their discovery consists in reducing the carbonic acid into carbonic oxide, so that the apparatus forms at the same time a carbonic oxide generator, in which the units of heat formed by the combustion of carbon to carbonic oxide, otherwise lost, are made use of, and the carbonic oxide is used as a heating gas. Rigaud also uses a double shaft furnace. One shaft is upright, and is charged in the usual way with ore and fuel. The other has an inclined position, and is in combination with the first under the hearth. It is only charged with coal. Metallic vapours come off with the gases escaping from the hearth, oxides probably being reduced also. Its temperature is only so high that the metallic vapours are condensed, and the liquid metal runs down the side channels, and is collected in an outside receiver. Steger considers the preparation of zinc in shaft furnaces possible if enough heat is produced for the reduction, and the zinc produced led over in an atmosphere of carbonic oxide into the cooled receiver for condensation in the liquid form. Steger has tried to discover whether by regulating the air current and the supply of coal the percentage of carbonic acid in the gas may be reduced so low that its action is immaterial. One of the most important conditions for producing an atmosphere rich in carbonic oxide consists in maintaining the highest possible temperature of combustion by means of a hot blast. With a blast temperature of about 1200°C. only a trace of carbonic acid is formed with the carbonic oxide. Clerc uses a blast heated nearly to the melting-point of iron on a cold mixture of zinc oxide and charcoal powder. The zinc is driven forward as zinc-dust, and at first flakes of zinc oxide are formed. Steger recommends, more recently, horizontal shaft ovens. In these furnaces the zinc ore, mixed with coal, is charged from above. The furnaces are then brought to a full-red heat by a very hot blast, and reduction ensues.

The question now to be solved is how to obtain the least possible quantity of carbonic acid, and have all the oxygen of the blast converted into carbonic oxide. Continuous working is not possible with these furnaces. Horizontal ovens are stated to be preferable for sanitary reasons.

Eichorn's method resembles Westman's in the choice of apparatus, but differs essentially in principle. Eichorn heats the oxides produced by the reduction of the carbonic acid again to a temperature sufficiently high to reduce them (Berg. und Hütt. Z. 1888, Nos. 43 and 44). For this purpose two shaft furnaces filled with coke are used, the temperature being maintained by the use of hot blast. These coke furnaces serve to store up heat and for reduction, while the Westman gas producers are only for condensation (Kovort, D. P. J. 272, 268, 312; S. C. I. 8, 545).

Hunicke also (Eng. Pat. 18024, 1888) proposes to get rid of the carbon dioxide in the gases by passing the vapours through heated charcoal, so that only carbonic oxide and zinc are left. The zinc is then condensed in suitable coolers; while Walsh (Eng. Pats. 8599, 1887, and 7181, 1889) states that carbon has no effect on carbon dioxides at temperatures below 1300°F.; but at 1400–1500°F. carbon converts carbon dioxide into the monoxide, which has no effect on zinc vapours. Walsh, therefore, proposes to pass the vapours over carbon at the latter temperature and to condense the zinc. The zinc oxide is reduced in a closed top cupola furnace, and the vapours passed through the heated carbon contained in a chamber attached to the furnace. The vapours are then passed through a condenser consisting of two parallel and horizontal iron pipes connected together with a series of vertical U-tubes, the condenser being maintained at such a temperature that the condensed zinc remains in the liquid condition.

The above references indicate the direction of experiments undertaken to solve the problem of smelting zinc in blast furnaces, but most of the processes described have partaken more of the character of large-scale experiments than commercial processes, and a thoroughly satisfactory solution has not yet been introduced.

Wet methods of extracting zinc. One of the most difficult problems connected with the metallurgy of zinc is that of the treatment of complex ores. These may contain, in the aggregate, very considerable proportions of metallic constituents, but in that a number of metals are present together the ores cannot be treated by ordinary methods. Such ores usually contain about 12 to 28 p.c. of zinc, and 5 to 15 p.c. of lead, together with a few p.c. of copper, some ounces of silver per ton, and frequently small proportions of other constituents. Various wet methods of extraction, usually connected with electro-deposition, have from time to time been suggested, and have been worked on a more or less considerable scale, though as yet usually without much commercial success. It is only after many trials that copper-refining by electro-deposition has, during the last decade, become a commercial success; and yet copper is worth more than double the price of zinc. The electro-motive force required for the deposition of copper is less than that necessary for zinc, and the strength of current that may be used with copper is greater. Thus electrolytic methods of extraction of zinc have to contend with the disadvantages of the comparatively low intrinsic value of the metal, and of comparatively slow deposition.

Where electro-deposition is employed, there are two methods open for extracting the zinc; in the first the ore itself may be used as anode; or, secondly, the ore may be roasted or treated with solvents to convert the zinc into a soluble form.

1. Luckow proposed to mix the ore with coke in order to render it a conductor, and to place it in an open chest in an electrolyte consisting of a somewhat strong and acid solution of common salt or chloride of zinc (20–30 p.c. Zn). The metal was deposited either upon a zinc plate or upon a cathode of coke. Higgs (Eng. Pat. 9158, 1886) proposed a similar method, but used magnesium chloride as electrolyte, and adopted special arrangements for collecting the evolved chlorine.

2. Many processes have been proposed for rendering the zinc in complex ores soluble, and in a number of these it is proposed to recover the zinc from solution by electro-deposition.

Lambotte and Doucet proposed to roast blende to oxide, dissolve in crude hydrochloric acid, precipitate the iron with chloride of lime and zinc oxide, and electrolyse the solution.

Parnell calcined complex ores to oxide, dissolved in dilute sulphuric acid, which was obtained as a by-product, precipitated the copper by metallic iron, and evaporated the liquor to a mud. Zinc sulphide was then added, and zinc oxide produced by heating the mixture strongly. The zinc oxide so obtained was sold to the smelters. Maxwell Lyte calcined the ore, and dissolved in hot dilute hydrochloric acid; the lead was allowed to separate as chloride on cooling, the iron precipitated by limestone, the copper with scrap iron, and the zinc as oxide by lime. Létrange was one of the earliest workers in the direction of electro-deposition of zinc; in this process blende was carefully roasted at low temperatures to produce zinc sulphate, which was dissolved with hot water and dilute sulphuric acid. The solution was then electrolysed, using an anode of lead (or carbon) and a cathode of zinc. The current used must have a high electro-motive force owing to the peroxidation of the surface of the lead.

Among the suggestions of the last few years the following are worthy of notice. In 1886 Lea and Hammond (Eng. Pat. 10868) suggested the use of hydrochloric acid as a solvent for roasted ores previous to electro-deposition, while in the same year Squire and Currie (Eng. Pats. 12249 and 12630) proposed the use of an alkaline solution for the same purpose, and in 1887 Watt patented (Eng. Pat. 6294) the application of dilute vegetable acids for a similar object. Again, Burghardt (Eng. Pat. 9886 and 13182, 1888; 659, 1889) proposed the use of an alkaline solution made by adding the roasted ore, previously mixed with 3 to 7 p.c. of powdered coal or charcoal, to melted caustic potash or soda. The mass was extracted with water, the zinc electrodeposited, and the alkali recovered to be used over again. Croselmire (Eng. Pat. 4286, 1888) proposed to mix the ground ore with clay, and form into perforated pressed bricks which are roasted into sulphate in kilns. The roasted mass is extracted with hot water and an equivalent of dilute sulphuric acid, air is blown through the liquors to precipitate iron and manganese, and, after settling, the clear liquor is electrolysed, or the zinc may be precipitated by soda ash. In 1889, also, Cunningham (Pat. 9987) again patented the use of an alkaline solution obtained by fusion with caustic soda.

Among methods of another class proposed for the treatment of complex zinc ores may be mentioned that of Perino (Eng. Pat. 10657, 1888) who fused the blende in clay retorts at 150° to 200°C. with nitrate of iron in the proportion of about 5 parts of nitrate of iron to 1 of zinc. The mass was extracted with water and a solution of zinc sulphate obtained. Arrangements were made for recovering the nitrate of iron. Siemens and Halske also (Eng. Pat. 3533, 1889) use ferric sulphate for extracting zinc from complex ores, while Seegall (Eng. Pat. 4871, 1889) employs a slightly acidulated solution of ferric chloride for the same purpose.

The complex ores of Leadville, U.S.A., containing 25 p.c. zinc, 15 p.c. lead, 20 p.c. iron, are roasted to sulphate, extracted with water; the residue chlorinised to complete the extraction of the zinc, and the zinc precipitated from the solutions as oxide (S. C. I. 7, 572). There is thus no lack of methods proposed for the extraction of zinc in the wet way, and much attention has been devoted to the subject, but at present it cannot be said that a satisfactory solution of the difficulty has been obtained, and none of the processes above mentioned have as yet met with extended application in the United Kingdom, whatever may have been their reported success elsewhere.

The methods adopted for the treatment of the complex ores of Freiberg are probably at least as successful as any of those above described. A splendid ore-dressing plant on the newest system was erected in 1890, and by systematic crushing and washing a very perfect separation of galena, blende, pyrites, &c., is obtained. The minerals so separated are then treated for the recovery of their respective metals.

Properties.—Zinc is a bluish-white metal, which at ordinary temperatures is brittle, and when pure exhibits a beautifully crystalline fracture. The presence of impurities usually renders the fracture closer in the grain and less brilliant. Zinc melts at 420° (433° Carnelley), and boils at the melting-point of silver. Its tensile strength varies greatly according to the mode of preparation; cast zinc has a tenacity of only 1·2 tons per square inch, while an annealed rod gave a tenacity of 7·9 tons per square inch, and zinc wire 10 tons per square inch. Its hardness is intermediate between that of tin and copper, being equal to 6 on Turner's Sclerometer and $2\frac{1}{2}$ on Moh's scale.

Though zinc is brittle at ordinary temperatures, and so tender above 200°C. that it can readily be crushed to powder, it can be rolled into sheet or drawn into wire at an intermediate temperature of about 100 to 150°. It is a remarkable fact that the metal when so treated retains its malleability in the cold. Zinc was first rolled early in the present century in Birmingham, and rolled zinc now forms one of the most important applications of the metal, the greater part of the zinc produced in Europe being used for this purpose. Commercial zinc always contains more or less lead and iron, together with traces of cadmium, arsenic, and sulphur, the lead being volatilised with the zinc in the process of manufacture. Dr. Kosmann has also found comparatively large quantities of thallium in commercial zinc (Chem. Zeit. 10, 762). It is not generally known that the presence of lead, which is objectionable in zinc to be used for the manufacture of the best qualities of strong brass, is an advantage in zinc that is to be rolled. As English zinc is generally nearly free from lead, it is usual to employ this variety for the production of alloys in which lead would be objectionable, while Continental zinc is imported for rolling. If the state of the market renders it advantageous to roll English zinc, this can be improved by the addition of a small proportion of lead. In addition to what is made here, about 20,000 tons of sheet zinc is annually imported into the United Kingdom. The density of zinc varies from 6·8 to about 7·2 according to the mode of preparation.

When heated in the air much above its melting-point, zinc readily burns with a brilliant greenish-white flame, producing the oxide (ZnO) which condenses in a bulky flocculent condition formerly known as 'philosopher's wool.' The white fume produced when casting brass or other zinc alloys that melt at a tolerably high temperature consists of zinc oxide. Though zinc is readily volatile, the oxide is fixed at all ordinary furnace temperatures. Zinc is not affected by dry air at ordinary temperatures, but tarnishes superficially in moist air. The metal is also not attacked by mineral lubricating oils, and of ordinary animal oils it is attacked most by sperm oil and least by lard oil (Redwood, S. C. I. 5, 362). Zinc, both pure and commercial, dissolves readily in alkalis and in nitric acid. Pure zinc is unattacked by water at the boiling-point, and is almost unaffected by ordinary acids either diluted or strong. Commercial zinc, on the other hand, decomposes boiling water with the evolution of hydrogen, and is readily attacked by diluted sulphuric acid and by hydrochloric acid either diluted or strong. Impure zinc when amalgamated resists the action of acids exactly like pure zinc, and hence the zinc plates used in electric batteries are amalgamated so as to prevent the loss due to 'local action.'

This difference in the behaviour of pure and impure zinc towards acids has attracted much attention from chemists since the fact was first pointed out by A. de la Rive in 1830. Among the more recent observations on the subject are those of Pullinger (C. J. 57, 815) and Weeren (Ber. 24, 1785).

Pullinger's conclusions are as follows:—Pure zinc with a perfectly smooth surface is not acted upon by dilute sulphuric acid that has been previously well boiled; pure zinc with a rough surface is readily acted upon, but less by acids that have been boiled than by those which have not. The presence of oxidising agents such as nitric acid, hydrogen peroxide, or electrolysed sulphuric acid, increases the rate of dissolution, while a reducing agent, such as hydriodic acid, almost entirely prevents dissolution; but reducing agents containing sulphur, such as sulphur dioxide, are without effect. It is not improbable that when zinc with a rough surface dissolves in dilute sulphuric acid the cause of dissolution is persulphuric acid, which acts catalytically, and in all probability *pure* dilute sulphuric acid would be without action upon metallic zinc, whether the surface of the latter be rough or smooth.

The solubility of impure zinc in diluted acids has been generally explained on the supposition that local electric currents are set up owing to the presence of the impurities, while with pure zinc no such currents are produced. Weeren, however, shows (*l.c.*) that the insolubility of pure zinc is due simply to the formation of a layer of condensed hydrogen on the surface of the metal, and thus the further action of the acid is stopped. Oxidising agents remove this film and assist dissolution; while in impure zinc the hydrogen, obeying ordinary electrical laws, is evolved from the surface of the impurities. The fact that dissolution is much promoted by simply brushing the surface of the metal, or by allowing the action to take place in a vacuum, appears to afford strong support of this view, which is also quite in harmony with the fact that pure zinc dissolves much more rapidly in boiling dilute sulphuric acid, when the ebullition of the liquid removes any hydrogen from the surface of the metal, than at 98° where no ebullition occurs. Pure zinc with a rough surface, as Pullinger has shown, dissolves much more readily in diluted sulphuric acid than the same metal when the surface is perfectly smooth. Weeren suggests from the above facts that the difference in the action of diluted sulphuric acid on pure and impure zinc is capable of a simple mechanical explanation.

The question of the corrosion of zinc sheet and pipes, and of articles coated with zinc, when in use, is of great commercial importance. In dry pure air, as for instance in parts far removed from manufactories and towns, zinc roofing, when properly attached, lasts almost indefinitely with only a surface oxidation. But in the neighbourhood of towns, and especially in the vicinity of chemical manufactories, commercial zinc is rapidly corroded and spoiled. The presence of the slightest trace of free sulphuric or hydrochloric acid in the drainage water is very prejudicial. The presence of copper in any form in contact with zinc, should also be carefully avoided. Thus Müller has shown (Ding. 269, 280), that the zinc pipes which carried the drainage water from the copper dome of the royal castle at Brunswick, were rapidly attacked and corroded, while similar pipes on the opposite side of the same building were unaffected. The explanation of this difference probably was that in the presence of ammonia or of acids in the atmosphere some copper was dissolved by the rain water, and this copper being afterwards deposited on the surface of the zinc, set up an electric action resulting in the destruction of the pipes.

The use of galvanised iron tanks for water-cisterns has led to much controversy, particularly in the colonies, as to the effect of such storage on the health of persons who drink the water so stored. According to Bunte, the use of zinc-coated iron water-pipes is not deleterious to health, and this view is supported by Dr. Ehmann, late director of the water supply of Würtemburg, and by Dr. Boardman, of Boston (S. C. I. 6, 557). But a strong feeling exists to the contrary, and, after careful inquiry, the use of galvanised tanks for drinking-water has been condemned in the British and French Navies. From the well-known properties of zinc it might be anticipated that some waters, which are either slightly acid or alkaline, would attack zinc vessels, while other waters might be almost without action. The presence of chlorides would probably also be prejudicial. It is not unlikely, therefore, that the differences in the action of water on zinc cisterns as noticed by various observers, is due in great measure to the character of the water. It is, however, certain that zinc or galvanised vessels should not be employed with acid waters.

Zinc-dust is employed somewhat largely as a reducing agent, and in the manufacture of fireworks. It is obtained, mixed with more or less oxide, in the distillation of the metal, or can be produced by crushing the metal in a mortar at a temperature somewhat below its melting-point.

In castings zinc takes a very sharp impression of the mould, and as it melts at a low temperature, it has been used to a considerable extent, especially in France, for the production of statuettes and other objects of great beauty, which are afterwards usually coloured or bronzed. The introduction of photo-engraving has also in recent years led to the use of considerable quantities of sheet zinc of special quality.

Galvanising. An important application of zinc, known as galvanising, was patented by Crawfurd in 1837. The object of the process is to coat the surface of iron with a thin layer of zinc, which protects the metal underneath from oxidation. In this respect zinc acts more perfectly than tin, which is negative to iron; in the case of tin plates the protection only lasts so long as the surface of the iron is covered with tin, but as soon as any portion of the iron is exposed to the action of the atmosphere oxidation proceeds more rapidly than in the absence of tin. Zinc, on the contrary, is more positive than iron, and thus, even though the coating of zinc may be removed in places, the protection continues so long as any zinc remains. Galvanised iron, however, cannot be used in contact with acids or alkalis, nor for the canning of fruits, meat, &c., on account of the action of vegetable acids and animal juices on the surface of the zinc.

The operation of galvanising is not in any way an electric process, as might be inferred from its name, but is simply a method of coating clean iron with zinc by immersion in a molten bath of the latter metal. Numerous patents have been obtained for suggested improvements in galvanising since Crawfurd introduced the process, particularly by Mallet and Morewood, but the old process is still almost universally adopted with a few improvements in details for saving of labour and the production of a better surface with a smaller consumption of zinc. Galvanising is conducted principally in the United Kingdom, and particularly in the neighbourhood of Birmingham and Wolverhampton.

The iron to be galvanised is received in the black state, coated with scale from the process of manufacture. Sheets are close annealed (*i.e.* annealed in large iron boxes, while carefully protected from access of air) to render them soft, but many other articles are treated without annealing. The scale is next removed by pickling in hydrochloric acid, which is used cold, or nearly cold, and which is contained in stone troughs. Tanks built of blue brick, set with sulphur joints, are also frequently used for containing the pickling acid. The strength of the acid depends on the character of the work; for wire 12 p.c. of real HCl is sufficient; for tubes, buckets, and general work an intermediate strength is best; while for sheets about 20 p.c. is generally used, and sometimes the undiluted muriatic acid of commerce (26 to 30 p.c.) is employed. By this method of working, pickling is usually complete in a few minutes; but on the Continent, where acid is dearer and economy is necessary, a dilute pickle is used, the water is heated, and the sheets are allowed to remain in the pickle for about two hours. The scale having been thus dissolved or loosened, the iron is washed with water, and, if necessary, rubbed with sand to complete the cleansing. The molten zinc is contained in a wrought-iron pot, the dimensions of which vary according to the character of the work to be done, and which is heated by means of a slow coke fire around the sides and under the bottom of the pot. The surface of the zinc is covered with powdered salammoniac, which acts as a flux, and when best sheets are being treated it is usual to add about 2 or 3 p.c. of tin to the bath so as to assist in the production of a crystalline appearance of 'spangle' on the surface. In other cases remelted zinc, *i.e.* zinc containing some tin and lead solder, is added to the bath for the same purpose. In galvanising sheets also it is usual to have a pair of rolls in the bath to guide the sheet in its passage through the zinc and to improve the surface. The consumption of zinc can be somewhat reduced, and the surface considerably improved, by the use of rolls or wire brushes as the sheet leaves the bath. Koffler and Breden (Eng. Pat. 12485, 1885; and 16674, 1888) have patented the use of wire brushes for this purpose; while Heathfield (Eng. Pat. 10089, 1886; and 1682, 1890) has introduced brushes which press evenly on the surface of the sheet as it leaves the bath, and he also adds fine wire brushes, together with improved rolls for feeding in the sheets. Corrugated sheets form a considerable portion of the trade; these are galvanised plain, and afterwards passed through corrugating machines in the cold. In galvanising wire, it is reeled through the pickle trough and the zinc-bath continuously, while netting is woven in the black, and afterwards reeled like wire. A continuous arrangement for this purpose has been patented by Vibart (Eng. Pat. 14297, 1889). The proportion of zinc taken up by the iron in galvanising varies considerably, being as high as 25 p.c. with moderately small wire, and less than one-fourth of this with many articles such as anchors, chains, and large elbows. In some galvanising works the sheets are pickled with hot diluted sulphuric acid, and the molten zinc is covered with zinc chloride instead of ammonium chloride; but the process above described is in much more general use.

The molten zinc gradually takes up iron

during the galvanising process, and forms an alloy which is heavier than zinc, and which sinks to the bottom of the bath. This is removed from time to time and cast in plates, which, when broken, exhibit a close-grained fracture with black spots. This alloy is known as 'hard zinc,' and contains from about 2 to 5 p.c. of metallic iron. It is usually re-melted at a higher temperature, when it separates into two portions, one being tolerably pure zinc. The other portion is much less fusible, and forms a crystalline or granular material of the colour of zinc; it is very friable, and frequently exhibits surface colourations of great beauty. In this form it is generally sold to the smelter, and contains about 7·5 p.c. of iron, though exceptionally compounds are produced which contain upwards of 25 p.c. of iron.

The ammonium chloride used as a flux in galvanising is gradually lost during the process, and fresh additions have to be made as required. This loss is doubtless due in part to volatilisation of the salt itself, but also to a reaction which takes place, whereby zinc chloride is formed and ammonia set free. It has recently been proposed to collect the fume of ammonium compounds evolved from the galvanising bath by suitable exhausting arrangements and scrubbers in which the gases are washed by diluted acid, and it is stated that such an arrangement not only very much improves the atmosphere of the manufactory, but actually yields a profit in working.

The result of the action of the ammonium chloride and of atmospheric oxygen on the molten zinc during galvanising is the production of a scum which is known as 'flux skimmings,' and which is removed from time to time. This material consists of chloride and oxide of zinc, together with some chloride of ammonium and dirt; it is usually sold to the smelters. Heathfield (Eng. Pat. 14411, 1885) has proposed to dissolve the chlorides in water and deposit the zinc electrically; while Richards (Eng. Pat. 13982, 1885) dissolves the oxide of zinc, together with the chlorides, in the minimum quantity of hydrochloric acid, and after evaporation electrolyses the concentrated solution of chloride of zinc.

The electrolytic method has also been applied to the treatment of the zinc scum obtained during desilverising, and Rosing states (Ding. 263, p. 87) that this method is the most suitable for the purpose of any process at present known. The powdered scum is spread on a lead plate at the bottom of a wooden vat which is filled with a solution of zinc sulphate. The lead plate acts as anode, and when the current is passed, zinc deposits on the cathode, and a corresponding weight of zinc is dissolved from the scum. When the surface zinc has been thus removed, the residual mass is dried and heated to redness in a cupellation furnace and again electrolysed.

The quantity of hydrochloric acid annually used for pickling in the country is very great, as a number of firms engaged in the galvanising trade each require some thousands of tons of commercial muriatic acid (26 to 30 p.c.) per annum, but no statistics on this point are available. When the works are situated near the sea the waste pickle is readily disposed of, but the Midland manufacturers have during the last few years met with increasing difficulty in getting rid of their waste acid. The nuisance has become intolerable, and costly litigation has been undertaken by the local corporations to enforce some efficient system of treatment. Hitherto the usual system has been that of neutralisation with lime and subsequent filtration, with or without subsequent roasting of the ferrous precipitate, to convert it into red oxide of iron. Turner has recently (Eng. Pat. 1889, 1890) introduced a method of recovering the hydrochloric acid, and the process is now in successful operation at three works in South Staffordshire. The waste liquor, which consists of an acid solution of ferrous chloride, contains slightly under 10 p.c. of iron and about 15 p.c. of acid, chiefly in combination. The liquor is allowed to trickle slowly into a fire-brick reverberatory furnace of special construction; this is connected with condensers for the acid, which are arranged in the ordinary way. A bath of concentrated ferrous chloride solution is maintained in the furnace and thus prevents leakage, as the saturated solution penetrates any crack, and solidifies in coming in contact with the cool exterior of the furnace. The ferrous chloride is more strongly heated near the firebridge, and decomposes thus:

$$2FeCl_2 + 2H_2O + O = 4HCl + Fe_2O_3.$$

Hydrochloric acid is thus recovered and used over again, while the ferric oxide is raked out of the furnace and used as fettling in the puddling process. The fuel consumption is about 4 cwt. of gas coke per ton of waste liquor treated.

When sulphuric acid is used for pickling, the solution is evaporated and crystallised to produce copperas (commercial ferrous sulphate), for which there is a limited demand. In a few instances the copperas is afterwards decomposed by heat for the production of rouge, and other varieties of bright-red ferric oxide.

Alloys of Zinc.

Zinc readily unites with most metals when the temperature is sufficiently raised to insure fusion. The *binary* alloys of zinc are generally white, crystalline, brittle materials, of limited importance. These alloys are usually of uniform composition; with lead and with bismuth zinc unites at a temperature above its melting-point, but the alloys separate on cooling into two distinct layers, the upper layer in each case consisting of nearly pure zinc. The most important series of binary alloys of zinc is the copper-zinc (or brass) series, which is separately described.

With *antimony*, zinc readily unites in all proportions; the resulting alloys are brittle, and exhibit a close-grained, dark-grey fracture when much antimony is present; when antimony is in excess, the surface of the alloys readily tarnishes during the process of casting, and the ingot becomes coated with a dark-grey crust of oxide. When the constituent metals are present in about equal proportions, surface colourations of great beauty can be obtained by oxidation, the tints obtainable including yellow, green, red, purple, and blue. A small proportion of antimony renders the surface colour of cast zinc distinctly more blue than usual, and with care the presence of 0·5 p.c. of antimony can be readily detected by this test. The usual colour of the surface of ingots, of equal parts of antimony and zinc, is a bright sky blue, and the alloy has the peculiar property of writing upon glass (Turner). Antimony zinc alloys are readily fusible, and in this respect the influence of antimony is quite different from that of arsenic or phosphorus, both of which raise the melting-point of zinc. Zinc antimony alloys have met with an application for the production of thermopiles, for which purpose they are well suited.

With *bismuth*, zinc unites when the metals are melted together, but on cooling the alloy separates into two layers, the upper consisting of zinc containing 2·4 p.c. of bismuth, while the lower layer consists of bismuth containing 8·6 to 14·3 p.c. of zinc. With *gold*, zinc forms a series of alloys which are pale yellow, with excess of gold, and greenish as the proportion of zinc increases; all these alloys are more or less brittle. In the production of jewellery part of the copper used in the preparation of the gold alloy is often replaced by brass, as the colour of the resulting gold can be thus improved, while the cost of the alloy is slightly reduced. The presence of much zinc renders the gold hard and difficult to work, and as the zinc is volatile at high temperatures this alloy is not suitable for use where the article has to be reheated during manufacture.

With *iron*, zinc forms a series of alloys which are generally white, hard, and brittle. With not more than 5 p.c. of iron the alloys are close-grained and darker in colour than pure zinc; such alloys are produced in the process of galvanising, and are known as 'hard zinc.' With more iron the character of the alloy varies according to the method of preparation. The ferriferous residue left on liquating 'hard zinc' is very friable, and readily crushes into a coarse dust, consisting of bright flakes or spangles; on the other hand, the material obtained by fusion is compact, white, hard, and brittle. The alloy of zinc and iron obtained by saturating zinc near to its temperature of volatilisation with iron, is not attracted by a magnet; it does not rust, nor give sparks by friction or blows. It is dense in structure, but is only semi-metallic in fracture, and contains about 22 p.c. of iron. These alloys have a somewhat important application in the preparation of 'delta metal,' and also of Aich, sterro, and Gedge's metal, all of which are yellow brasses containing about 60 p.c. of copper and nearly 40 p.c. of zinc. The addition of iron to these brasses, first suggested by Keir in 1779, imparts special hardness, toughness, tenacity, and wearing properties, while the alloy can be rolled either hot or cold, and the constituents of the mixture are relatively cheap. The proportion of iron present usually varies from about $\frac{1}{4}$ to 4 p.c., according to the purpose for which the alloy is to be applied. The necessary zinc-iron alloy can be prepared by one of the following methods:

1. By immersing clean iron wire, or sheet, in a bath of molten zinc heated to near its boiling-point. The addition of a little charcoal and some solid ammonium chloride assists the action. Where the presence of a little tin in the alloy is not objectionable (as for sterro-metal) a convenient method is to employ clean tin-plate scrap; the coating of tin readily unites with the zinc and leaves a clean surface of iron exposed to the action of the molten metal.

2. In order to reduce the waste of zinc usually accompanying the production of such alloys, a zinc of high boiling-point may be advantageously used in some cases. Bull (Eng. Pat. 4086, 1888) has proposed the addition of phosphorus or arsenic for this purpose, while the addition of a little copper to the zinc assists the action without the introduction of any injurious constituent.

3. Alloys rich in iron can also be obtained by liquating the 'hard zinc' from galvanising works, and heating the ferriferous residue strongly in a closed crucible. The excess of zinc is volatilised, and the percentage of iron increases with the temperature employed. The alloys actually used in practice contain from about 7 to nearly 30 p.c. of metallic iron.

With *lead*, zinc readily combines when the two metals are melted together, but on cooling the mixture, or allowing it to remain at rest, the zinc collects as a layer at the upper surface, while the lead is found at the bottom of the mass. The metals are, however, neither quite pure, for the lead on cooling retains 1·6 p.c. of zinc, while the zinc retains 1·2 p.c. of lead (Percy, Metallurgy, 90). These proportions vary somewhat according to the method of treatment. Thus E. Krant has examined the behaviour of zinc containing lead on remelting (S. C. I. 5, 537). The sample was melted, well mixed, and a quantity removed and granulated. The residue was allowed to cool slowly, and the top, middle, and bottom of the mass separately analysed. The top contained 0·943 p.c. of lead, the middle 2·847 p.c., and a small quantity at the bottom as much as 4·121 p.c.; while the original zinc only contained 1·543 p.c. of lead. In these experiments only 2 kilos of metal was employed, and on the large scale the separation of the two metals is still more complete.

The rolled zinc of commerce is a nearly saturated solution of lead in zinc, and usually contains about 1 p.c. of lead. An excess of lead injuriously affects the rolling properties; hence it is usual when rolling Continental zinc to remelt it in a reverberatory furnace with an inclined bed. The metal is allowed to remain fluid at a temperature a little above its melting-point, and the zinc is ladled off from the top from time to time. The excess of lead separates and collects as a layer in the lower end or 'sump' of the furnace, beneath the zinc, and is removed at suitable intervals.

On strongly heating lead-zinc alloys, the excess of zinc is at first volatilised, but as the temperature rises both lead and zinc distil over together. This curious volatility of lead in the presence of zinc is doubtless the cause of the occurrence of lead in commercial zinc, obtained from ores containing lead. The presence of a small proportion of zinc in commercial lead communicates hardness and allows the lead to receive a good polish without destroying its malleability.

With *mercury*, zinc readily unites to form a series of white brittle amalgams which become pasty when mercury is in excess. Zinc amalgams are easily obtained by mixing mercury with molten zinc, or by adding zinc to mercury heated nearly to its boiling-point. Zinc plates for galvanic batteries are coated with mercury by first cleaning the surface of the zinc with dilute sulphuric acid and then rubbing the mercury over the clean surface. An amalgam of zinc and tin is used on the rubbers of frictional electrical machines. On the literature of zinc-amalgams *v.* S. C. I. 9, 512.

With *silver*, zinc does not very rapidly unite at the melting-point of the latter, but at higher temperatures the metals readily combine, forming a series of alloys which are whiter than zinc, and the use of which has been proposed for coinage and other purposes. With 5, 10, or 20 p.c. of zinc, silver forms white ductile alloys, which can be rolled like standard silver, and which are more fusible than the corresponding copper alloys (Percy, Gold and Silver, 169–171).

With *tin*, zinc readily unites in all proportions, the resulting alloys being generally harder than tin but softer than zinc. The colour of the alloys is in all cases white, and the fracture is crystalline, though its appearance varies with the mode of preparation. The alloys of tin and zinc are not quite uniform in composition, as the tin tends to separate and collect at the bottom on cooling. Tin zinc alloys are used for castings of patterns for ornamental purposes. A detailed description of these alloys, based on the work of Guettier and Rudberg, is given in Hiorns' Mixed Metals, 249–253.

German Silver, Brass, &c.

In addition to the binary and other zinc alloys above mentioned, zinc enters into the composition of a number of alloys containing three or more metals, of which the following are the most important.

German silver (also known as Nickel Silver, Packfong, White Copper, Electrum, Nevada Silver, &c.) consists of copper, zinc, and nickel. It is an alloy of white, or nearly white colour, of high tenacity, and capable of being cast, rolled, spun, and otherwise worked. One of its most important properties is its relative permanence in the air, and this has led to the use of the alloy on a very extensive scale. It usually contains about 60 p.c. of copper, the proportions of zinc and nickel varying according to the price and use of the alloy; the zinc is seldom less than 14 or more than 30 p.c. of the whole. For castings a little lead is frequently added. Generally an alloy of about equal weights of zinc and nickel is first prepared, and to this 'temper' the necessary quantities of copper and brass are added to give the required composition. A good description of the copper-nickel-zinc alloys will be found in Hiorns' Mixed Metals, 235–248.

Part of the tin in *gun metal* and in *bearing metal* is frequently replaced by zinc, as it is found that the density and wearing properties of the alloy is thereby increased (*v. Bronze*, art. Tin). For the same reason the bronze coinage of this country contains 1 p.c. of zinc. Zinc is also present in some varieties of aluminium bronze, and in phosphor bronze, manganese bronze, and other similar alloys. The 'Biddery Ware' manufactured in India usually contains about 90 p.c. of zinc together with copper, lead, and tin in different proportions.

Copper alloys—Brass. *History.*—Although the word brass frequently occurs in the Old Testament, there is little evidence that an alloy of zinc and copper was known in these early times, unless, indeed, the suggestion be accepted that brass was sometimes accidentally produced in the manufacture of copper. The word translated 'brass' might equally well be rendered copper or bronze, both of which were in common use for a considerable period before the introduction of copper-zinc alloys (*v. Bronze*, art. Tin).

There is abundant evidence, however, that brass was known to the Romans about the beginning of the Christian era; that it was used for coinage purposes, and that it formed one of the yellow alloys known as *orichalcum*. The analytical and historical evidence on these points have been admirably summarised by Dr. Percy (Metallurgy, i. 518–528). In the middle ages the Germans were famous for the production of brass, which was imported into this country chiefly in the form of sheet or *latten*, which was employed for the 'brasses' of churches, particularly in the Eastern counties. Over 4,000 such brasses are known to exist in various churches &c. in the United Kingdom, which is far richer in this respect than any other country. The first brass manufactory in England is stated to have been erected by a German in Surrey about the middle of the seventeenth century. Brass works were started in Bristol in 1702; while the first works for making brass in Birmingham (now the centre of the brass trade) were erected about 1740 by Turner. Up till the middle of last century the only method used in the production of brass was the calamine, or cementation, process, in which copper, in the form of bean shot or sheet, was heated in crucibles in contact with calamine and carbon, with the result that zinc was liberated and volatilised, being afterwards absorbed by the copper. The brass thus produced was then melted down and cast. This process was slow and laborious, and only yielded a brass tolerably rich in copper. In 1781 James Emerson patented the direct production of brass from copper and zinc, though there is evidence that the method had been previously used to a limited extent. The calamine process has been gradually superseded by the direct method of production, so that the last calamine brass works in this country was closed about 1850. Some of the most important factors in the development of the brass trade have been the introduction of rolling mills in the early part of last century, with the subsequent application of powerful machinery; the application of the stamp and die in 1769, whereby articles were produced more rapidly, with better finish, and with less metal than by the old process of casting; the introduction of gas fittings in the early part of the present century; the use of brass and copper tubes in locomotives and marine engines; the introduction of yellow metal sheathing; and the extended use of engineers' brass work and steam and water fittings. These and many other circumstances have resulted in an enormous development of the brass trade during the last half-century, so that it is believed there are employed at present in the brass trade of Birmingham alone over 30,000 persons (male and female), while the consumption of metal is valued at 2½ millions sterling. Owing to the relatively low price of copper in recent years the value of the metal used has remained about stationary, while the actual weight used has nearly doubled between 1865 and 1890. The price of common castings in brass has been reduced from 11*d.* per pound in 1865 to 7½*d.* in 1890; while the average wages, particularly of the ordinary workman, have considerably increased. An interesting pamphlet of 42 pages, entitled 'A Short History of the Brass Trade,' has been issued by Mr. J. W. Davis, secretary to the National Brass Workers' Association, since the above was written. *V.* also Ency. Brit., art. 'Brasses'; Thompson, Hist. of Chemistry, i. 55, 62, &c.; Midland Hardware District, 226–240; Percy, Metallurgy, 504; Holzapffel's Mechanical Manipulations, 312; Useful Metals and their Alloys, 566.

General properties of zinc-copper alloys.—Zinc and copper unite in all proportions, the resulting alloys being of remarkably uniform composition throughout the mass (Laurie, C. J. 53, 106; 55, 677). The experiments of Tilden S. C. I. 9, 84) also show the great uniformity in composition of commercial sheet brass, though on the other hand Hiorns (Mixed Metals, 107) gives analyses showing the copper to be less at the top than at the bottom of ingots of cast brass. The alloys containing upwards of 80 p.c. of copper are red or red-yellow in colour; those containing less than 48 p.c. of copper are grey or white; the intermediate alloys are yellow. The hardness of the alloys is usually greater, while the melting-point is lower, than that calculated from the mean of the constituents. The addition of zinc to copper produces remarkable alterations in the working properties of the product, varying, however, with the proportion of zinc present. Thus, pure copper can be rolled hot or cold, though in the latter case frequent annealing is necessary, and rolling hot is much cheaper and more expeditious. The addition of only a trace of zinc renders copper incapable of being rolled when hot, though it does not interfere with the malleability of the metal when cold. Hence all alloys which contain from about 62 to 100 parts of copper p.c., and the residue zinc, cannot be rolled hot, but, when necessary, are rolled cold with repeated annealing. But alloys with about 60 p.c. of copper can be rolled either hot or cold, and the cost of production is thus reduced. These alloys are, however, less ductile and tough than those which contain more copper, and are only suitable for use when moderate strength and toughness are required. The alloy of 60 parts of copper and 40 of zinc was patented by Muntz for the production of sheathing for wooden ships, and is now largely prepared under the name of 'yellow metal,' for the production of the cheaper varieties of brass sheet, tubes, and wire. The standard size of yellow metal sheets is 14 by 48 inches, and the thickness is returned according to the Birmingham metal gauge. Alloys containing about 50 p.c. of copper are light yellow in colour; but cannot be rolled either hot or cold. The chief application of alloys containing rather more than half their weight of copper is for the production of solder for use with copper, brass, &c. These alloys form what is usually known as 'hard' solder, in contradistinction to lead-tin alloys or 'soft' solder. But in the brass trade different varieties of solder are used, containing from about 49 to 56 per cent. of copper, according to the temperature to be employed. The solders containing more copper are called 'hard,' and those with more zinc 'soft.' The solder most commonly employed contains about 51 p.c. of copper, and is usually sold in the form of powder, which is prepared by heating a mass of the alloy to a temperature just below its melting-point, when it is struck a sharp blow with a mallet. At this temperature the alloy is very friable, and readily crumbles into powder when treated as above described.

With more than 50 p.c. of zinc the alloys lose their yellow colour and become white, brittle, and more fusible. Though all these white alloys are brittle when hot or when cold, they can usually be laminated at some intermediate temperature, and in this respect they resemble zinc. This proper temperature varies according to the proportion of copper present, being as low as 150° in zinc, and at a red heat, probably about 600°C., in yellow metal. As the copper increases beyond 60 p.c., as before explained, brass can no longer be rolled hot, but is laminated in the cold with repeated annealing.

According to Mallet (Construction of Artillery, 82), the alloy $CuZn_2$, containing about 33 p.c. copper and 67 p.c. zinc, is used for watchmakers' brass, and possesses the greatest tenacity of the whole series. This statement has been copied into all the well-known works on the subject, but it is evidently an error. Laurie has shown by his investigations on the electro-motive force of zinc-copper alloys (see above) that only one definite alloy exists in this series. This compound is white, hard, and brittle, and corresponds very closely in composition to Mallet's alloy above mentioned. All other zinc-copper alloys may be considered as solidified solutions of this definite compound in excess of one or other of the constituent metals. The definite alloy itself is hard, brittle, and of little or no practical value; but by its union with various proportions of copper, which alone is too soft, a whole series of alloys is obtained which possess most valuable and wonderfully graduated properties.

The following classification of the commercial varieties of brass, based upon the method of manufacture and proportion of copper, will serve as a general guide to the composition of these alloys; though for various reasons the proportions of the constituents are liable to some variations according to the requirements of the trade.

Cast brass. All brass is now made by melting together copper and zinc, but the term 'cast brass' is applied when the article to be made receives its form in the mould, and does not require to be afterwards rolled, drawn, hammered, or spun. For this purpose the charge is melted in clay crucibles, which usually contain about 90 lbs. of metal, and which are heated in small wind furnaces by coke. Generally each furnace contains but one pot, but sometimes two or four pots are placed in a single furnace, which is made proportionately larger in such cases. Sometimes also plumbago crucibles are employed, but as a rule in Birmingham clay crucibles are used for brass, and plumbago for bronze castings. In practice it is necessary to add a quantity of scrap brass to the charge, and this is generally introduced first into the red-hot crucible together with a small quantity of flux, which is added to remove the oxide and dirt adhering to the scrap. When only new metal is used the flux is either much reduced or altogether omitted. The fluxes most commonly employed are ground fluor spar, together with more or less glass, and *sal enixum* or acid sulphate of potash. When the scrap is hot the copper is charged into the crucible, usually in the form of ingots, though occasionally bean shot copper is used. After the copper has thoroughly melted, the zinc is cautiously added in as large pieces as possible. The use of large pieces of zinc reduces the loss, and moderates the violence of the combination. In any case considerable heat is produced by the union of zinc and copper, and some of the zinc burns with a dazzling brilliancy. After allowing the crucible to remain in the furnace a short time to allow the metal to become sufficiently fluid, it is poured into moulds, which for cast brass are generally of 'green' sand. While the brass is hot, zinc gradually volatilises and burns at the mouth of the crucible, forming zinc oxide; this produces the white fume which fills the casting house while the metal is being poured, and as a protection against the deleterious effects of inhaling the fume it is customary for the workman to keep his mouth and nostrils covered with a cloth. When the metal has set, the castings are turned out and dipped while warm into water, which detaches most of the adhering sand; the processes of dressing, grinding, polishing, dipping, and burnishing are necessary to give the required surface, while the finished article is lacquered to preserve it against atmospheric influences. The proportion of copper in cast brass varies considerably according to the purpose for which it is required; in some cases cheapness is of prime importance, in others the metal must 'dip' well when immersed in acid, while not unfrequently the shade of colour of the resulting alloy is of the utmost moment. Best cast brass generally contains from 70 to 75 p.c. of copper; ordinary good English brass 66·6 p.c. (*i.e.* 2 of copper to 1 of zinc); while common cast brass contains about 62 p.c. of copper. A little lead is generally added in preparing cast brass; this gives sounder castings and produces a metal which turns much better in the lathe than ordinary brass. Although not unfrequently as much as 2 p.c. of lead is added to the charge, most of this is removed by oxidation and usually only about 0·3 to 0·5 p.c. remains. The loss of metal in melting and casting is usually about 5 p.c., but this is greater when much small scrap is used. It may be added that in the preparation of cast brass it is not so necessary to insure the absence of very small quantities of metals such as antimony, bismuth, and silver as is the case when the alloy has afterwards to be rolled or drawn. When special ductility or malleability is required in the final product, it is of the utmost importance that the purest obtainable materials should be employed.

Sheet brass. Probably the most important application of brass is for the production of sheets, as sheet brass is not only needed for a multitude of useful and ornamental purposes itself, but it forms the starting-point for the manufacture of the greater part of the brass wire and tubing that is dealt with in commerce.

For the production of 'yellow metal' it is customary in the neighbourhood of Swansea, and occasionally elsewhere, to prepare the alloy by melting copper on the bed of a small reverberatory furnace and adding the requisite quantity of zinc. But in preparing other varieties of sheet brass it is usual to employ clay crucibles heated in coke fires as described for cast brass. The crucibles are, however, generally somewhat larger, and hold about 120 lbs. of metal. In either case the alloy when melted is cast in iron moulds into flat bars, varying in size, but of which one about 4½ in. × ¾ in. × 90 in. may be taken as an example. These are known as 'strips' and the operation is known as 'strip casting.'

The strips are then 'broken down' by being passed cold through a pair of rolls, the operation being repeated as often as the metal will allow. The work done upon the metal soon causes it to become hard, and if the rolling were continued the strip would readily develop cracks. To obviate this the metal is annealed at a red heat and the surface is cleaned from oxide by pickling in dilute sulphuric acid. After washing with water, the operations of rolling, annealing, pickling, and washing are repeated, in order, until the desired shape and thickness are obtained. Turner has recently shown (C. N. 63, 227, 64, 143) that the use of impure washing water containing chlorides leads to the production of copper-red stains and smears, on the surface of the finished brass, which are a cause of frequent loss and trouble. As sheet brass is used for so many purposes, its composition varies over a wide range, extending in fact from a mere trace to 40 p.c. of zinc.

Since the ductility of the alloy increases with the proportion of copper, alloys such as best red brass, gilding metal, and percussion-cap metal contain from 80 to 96 p.c. of copper. Dutch metal contains 80 to 85 p.c.; Prince's metal, 75 p.c.; best English sheet brass, 70 to 72 p.c.; ordinary, 66·6 p.c.; common, 63 p.c.; and yellow metal, 60 p.c. As already explained, this last alloy, though somewhat deficient in ductility and toughness, possesses the great advantage that it can be rolled either hot or cold. White metal alloys are used in the form of sheet to a limited extent, and these contain less than 50 p.c. of copper. The cheaper alloys, rich in zinc, do not 'stand the fire' so well in soldering, and it is not usual to solder anything containing less than 60 p.c. copper. Even with this composition a special soft solder has to be employed, while red brass stands the fire best, and can be used with the hardest solder.

Brass wire is made from sheet brass, the sheet of suitable thickness being slit into thin strips by cutters, and the strips are then drawn into wire at the draw bench. The chief varieties of wire arranged in order of ductility are as follows:—Red metal, Prince's metal, ordinary, common, and yellow metal. The first two of these were formerly used in the button trade, as in soldering on the shanks with hard solder they 'stood the fire' well. The other varieties can all be soldered with suitable solder of low melting-point, but the difficulty of soldering increases with the proportion of zinc.

Brass tubes. There are two principal methods of producing brass tubes. By the original process, which is still largely employed, sheet brass of the required composition and thickness is cut into strips of the necessary length; the strips are then drawn through a die, which imparts a circular shape, and the edges are soldered together by the use of powdered solder and borax made into a cream with water. Small tubes are soldered by being drawn through a small furnace fired with small coal or coke, but large tubes are now generally united by the use of a gas blowpipe, which gives a local and easily regulated heat. In the second and more modern method of manufacture brass tubes are solid-drawn, and thus the operation of soldering is dispensed with. This process is chiefly employed for large tubes and for tubes of special quality, as the soldered joint in tubes made in the ordinary way is always more brittle than the rest of the material. For solid-drawn brass tubes a short hollow cylinder of metal is cast in suitable moulds, and by drawing on a mandril, with frequent annealings, this hollow cylinder is gradually elongated to the required dimensions. Ornamental patterns on brass tubes when parallel with the length of the tube are produced by passing the plain tubes through a set of suitably arranged rolls, on the surface of which the desired pattern is cut.

But when the pattern is of a spiral form it is usual to draw the plain tube through a die of the requisite shape, arrangements being made for either the tube or the die to rotate during the operation. Best drawn tubes for locomotives and similar purposes contain 70 to 72 p.c. of copper; the composition of other tubes varies according to the quality of the sheet brass used in the process of manufacture.

Colouring of brass. A considerable proportion of the goods originally made of brass are so coloured before passing into commerce that the tint of the metal itself is no longer to be recognised. The most important applications of colouring are the following:—Bronzing in various shades, such as black, grey, red, green, &c.; lacquering in many shades; and bright colouring with highly coloured, transparent lacquers. These processes of colouring may be divided into two classes according as to whether they are conducted before or during the operation of lacquering.

As has been pointed out by Löwenherz, a variety of shades of colour can be obtained by carefully heating bright clean brass to definite and regulated temperatures. These colours so produced are formed in the following order:

1. Orange yellow.
2. Clear golden yellow.
3. Orange gold.
4. Dark gold.
5. Brown gold.
6. Rose-red gold.
7. Violet-rose red.
8. Clear rose.
9. Steel white.

Some of the colours are of great firmness and beauty, and the process is full of promise for special purposes, but has not hitherto been successfully adopted on any considerable scale.

The methods of bronzing, applied before lacquering, include the following:

Copper bronzing. To develop a copper-coloured surface on brass the metal may be cautiously rubbed with hydrochloric acid, or, still better, it may be immersed in a slightly acid dilute solution of copper nitrate until the desired depth of colour is obtained. To produce a dark copper-bronze colour, treat as above, and blacken the surface with plumbago before lacquering.

Grey bronze. A cheap grey bronze is produced by rubbing with plumbago and using a nearly colourless lacquer. A more permanent grey bronze is produced by the use of a solution of arsenic trioxide in hydrochloric acid; the addition of iron salts improves the effect. For common work, which is *not soldered*, an aqueous solution of mercuric chloride rendered acid with vinegar is frequently used.

Black bronze. The very beautiful and permanent black bronze used for mathematical and scientific instruments is produced by the application of a dilute aqueous solution of platinum perchloride which was introduced for this purpose about the year 1860.

Green bronze. A cheap green bronze which was formerly much in favour was obtained by the use of plumbago followed by a transparent yellow lacquer.

Ordinary lacquer is a solution of shellac in proof spirit, but other gums and solvents are also used. A colourless 'dip' lacquer (*i.e.* one in which the articles may be dipped, instead of the lacquer being applied by means of a brush to the warm surface as usual) is made by dissolving nitro-cellulose in amyl-acetate. For ordinary purposes many shades of lacquer from colourless, through yellow, to brown are regularly employed. For the cheaper kinds of bronzing special bronze lacquers of a variety of colours are used; and in addition richly coloured transparent lacquers of numerous shades are produced for the manufacture of brightly coloured thin sheet metal for ornamental purposes. In this branch of manufacture the use of aniline derivatives has led to numerous recent improvements.[1]

T. T.

Zinc oxide ZnO. This substance, the *nix alba*, 'philosophical wool,' or 'flowers of zinc' of the alchemists, the *tutia* or *pompholyx* of the ancients, is known in commerce as 'zinc-white,' and is prepared by burning zinc and leading the fumes into tubes or chambers, where it condenses. It is occasionally found crystallised in zinc- and brass-melting furnaces, and occurs native in orange-yellow hexagonal crystals;

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[1] Since the above was written, Hiorns has published a useful handbook on Metal Colouring.

similar hemimorphous pyramids, of sp.gr. 5·782, may be obtained by heating the nitrate (Brügelmann).

Zinc white is used as a paint instead of white lead, and for pharmaceutical purposes. The zinc oxide of pharmacy is prepared either by burning the metal or by precipitating zinc sulphate with a hot solution of sodium carbonate, and heating the dried carbonate to expel carbon dioxide.

Zinc oxide is a white powder of sp.gr. 5·6, which, on heating, becomes lemon-yellow, but on cooling again becomes white. When strongly heated in the oxyhydrogen flame it emits an intense white light, and is seen to phosphoresce when cooled in the dark. The character of the light emitted by incandescent zinc oxide has been examined by E. L. Nichols and B. W. Snow (P. M. [5] 32, 420, and [5] 33, 19).

Zinc chloride $ZnCl_2$, the *oleum lapidis calaminaris* of Glauber, who first described it in 1648, may be prepared in the anhydrous state by distilling zinc oxide with sal-ammoniac, forming the 'butter of zinc' of Hellot; by distilling zinc with corrosive sublimate (Pott); by the action of chlorine on the metal (Westrumb), or by heating dehydrated zinc sulphate with calcium chloride (Persoz).

Anhydrous zinc chloride is a greyish white, wax-like substance, of sp.gr. 2·75; it melts at about 110°, and may be sublimed or distilled unchanged. It is very deliquescent, and is readily soluble in alcohol and ether. It is employed in the laboratory to remove the elements of water from organic substances.

On the large scale it is usually obtained by placing scrap zinc in a stone, cast-iron, or wooden vessel containing hydrochloric acid. The solution is neutralised with sodium carbonate, warmed to 40° or 50°, and mixed with bleaching powder to precipitate iron and manganese. The clear zinc chloride solution is siphoned off and boiled down in enamelled iron pots. The evaporation is continued until the liquor is heated to 230° or 240°C., a little potassium chlorate is added to oxidise any organic matter, and some pure hydrochloric acid carefully poured into the hot solution to dissolve any basic salt. The mass is then allowed to solidify, the agitation being kept up all the time, and while still warm it is packed in iron drums of 30 to 50 kilos capacity, which are at once closed air-tight.

Zinc chloride comes into pharmacy in the form of rods or tablets. It is a powerful caustic, distinguished by its property of burning deeply and not spreading sidewise, like many others. It is applied in substance, or made into a paste with starch or gypsum, to cancers, sloughing or unhealthy sores, and nævi (Lauder Brunton). A solution of zinc chloride, in the proportion of 1 lb. of the salt to 5 gallons of water, was patented by Sir W. Burnett (No. 7747, 1838) for the preservation of timber, and such a solution is still occasionally used for disinfecting and deodorising.

Zinc chloride is also employed for weighting cotton goods. A solution of sp.gr. 1·7, boiled with excess of oxide, forms an oxychloride $ZnCl_2.3ZnO.4H_2O$, which dissolves silk, and may be used for separating this fibre from wool. Zinc oxychlorides are also used as pigments, as cements, and for making artificial teeth. Solutions of zinc chloride were also employed by Mercer for treating cotton in the operation of 'mercerising' (*v.* CELLULOSE).

A solution of zinc ammonium chloride is used in soldering for the purpose of removing oxide from the surface of the metals.

Zinc bromide $ZnBr_2$ is readily made by digesting granulated zinc with bromine water. It resembles the chloride, and is used to a small extent in medicine in the treatment of epilepsy.

Zinc iodide ZnI_2 is also employed in medicine, as an application to enlarged tonsils and in the form of ointment to reduce swellings. It is also administered internally in cases of scrofula, chorea, and hysteria. It has found a limited application in photography. For preparation *v.* IODINE.

Zinc sulphate $ZnSO_4$. This salt appears to have been first described by Basil Valentine under the name which it still bears, of 'white vitriol,' although it is probable that it was known long before his time. It was obtained, on a manufacturing scale, as far back as the 16th century, by lixiviating roasted zinc sulphide by means of water, and crystallising the solution—a method still practised. Native-zinc sulphate or *goslarite* is occasionally found in zinc mines, being probably formed by the oxidation of zinc sulphide.

Zinc sulphate separates from its solution at the ordinary temperature in right rhombic prisms, isomorphous with magnesium sulphate, and of the composition $ZnSO_4.7H_2O$; sp.gr. 1·964 (Thorpe and Watts). It has a strong metallic styptic taste, and effervesces slightly in dry air. According to Poggiale, 100 parts of water dissolve the following amounts of zinc sulphate at different temperatures:—

	$ZnSO_4.7H_2O$	Anhydrous salt
10°	138·2	48·3
20°	161·5	53·1
30°	191·0	58·5
50°	263·8	68·7
100°	653·6	95·6

The solution has an acid reaction and is poisonous. The salt is insoluble in absolute alcohol.

A hexhydrated salt $ZnSO_4.6H_2O$ is obtained by crystallising the solution at 40°; sp.gr. 2·072 (Thorpe and Watts); a pentahydrated salt $ZnSO_4.5H_2O$ by boiling the salt with alcohol of sp.gr. 0·825 (sp.gr. 2·206 Thorpe and Watts); a dehydrated salt by pouring a cold saturated solution of zinc sulphate into strong sulphuric acid, and washing the precipitate with absolute alcohol until free from uncombined acid; sp.gr. 2·958 (Thorpe and Watts). The monohydrated salt is formed by heating the heptahydrated salt to 110° until it ceases to lose weight; sp.gr. 3·284 (Thorpe and Watts). The anhydrous salt is obtained by heating the heptahydrate to 300°; sp.gr. 3·62 (Thorpe and Watts). At a red heat all the sulphates are decomposed, yielding a residue of zinc oxide.

Zinc sulphate is used in dyeing and calico-printing, in the manufacture of varnishes and drying oils for painting, for the preparation of zinc white and other zinc compounds, and in pharmacy as an astringent, and in lotions, washes, and gargles. It is also occasionally employed as an emetic, and in the treatment of convulsive diseases. A number of basic sulphates, formed by digesting the oxide or hydrate with strong solutions of zinc vitriol, or precipitating such solutions with varying quantities of potash, can be formed.

Zinc sulphate combines with ammonia and with other sulphates to form double salts.

Zinc carbonate $ZnCO_3$ occurs native as *calamine* or *zinc spar*. It can be formed artificially by adding zinc sulphate solution to a solution of acid sodium carbonate. When the normal carbonate is employed, basic zinc carbonates are formed, the proportion of zinc oxide varying with the temperature and dilution of the solutions. The *zinci carbonas* of the British Pharmacopœia has the composition $ZnCO_3(ZnO)_2.3H_2O$. At a red heat it loses carbon dioxide and forms zinc oxide.

Zinc chromate *v. Chromium.*

Zinc acetate and **valerianate** are also employed in medicine for the same purpose as the sulphate, and also as tonics. The former salt is also used in dyeing, and is usually prepared by mixing lead acetate and zinc sulphate solutions.

Zinc phosphide Zn_3P_2 is obtained as crystalline friable mass with metallic lustre, by heating zinc in phosphorus vapour in an atmosphere of dry hydrogen. It is used in medicine in place of phosphorus.

Zinc sulphide ZnS, as blende, is one of the most important ores of zinc. Its value as an ore of zinc was first demonstrated by Brandt in 1735; it was formerly regarded as a worthless lead ore, *galena inanis*. It is found crystallised in forms derived from the regular system, usually of a red, brown, or black colour, due to the presence of foreign metals. Occasionally it is met with of a light-yellow colour; sp.gr. 3·5-4·2.

It is obtained artificially as a white amorphous precipitate by adding an alkaline sulphide to a solution of a zinc salt. It is soluble in dilute mineral acids, but is insoluble in acetic acid. When heated in a stream of sulphuretted hydrogen, it forms hexagonal crystals identical in form with a naturally occurring variety known as *wurtzite*.

Zinc sulphide, or a mixture of zinc sulphide and oxide, is used as a pigment. Griffiths' 'patent zinc white' is obtained by the addition of a soluble sulphide to zinc chloride or sulphate solution, drying the precipitate, and calcining it. It is raked out whilst hot into cold water, and levigated (S. C. I. 4, 564). See also Griffith's Eng. Pat. 750, 1883; Knight, Eng. Pat. 16,220, 1884; J. B. Spence, Eng. Pat. 13,462, 1885; 14,128, 1885.

Zinc orthosilicate Zn_2SiO_4 occurs native as *Willemite*. *Siliceous calamine*, used to some extent as an ore of zinc, is a hydrated orthosilicate $Zn_2SiO_4.H_2O$. It is found in unsymmetrically-terminated rhombic prisms, and, like tourmalin, boracite, sugar, and other unsymmetrical crystals, it is pyro-electric—that is, on warming, one end becomes positively, the other negatively, electrified.

For methods of detecting and estimating zinc *v.* Analysis.

ZINC BLENDE *v.* Zinc.

ZINC-DUST (VALUATION OF). Klemp has devised a process for the above purpose which depends on the power of zinc to reduce potassium iodate to potassium iodide in an alkaline solution. When the solution is afterwards acidified, iodine is liberated by the interaction of the iodic and hydriodic acids, and is distilled off from the reaction mixture into potassium iodide solution, and titrated with thiosulphate. The details of the method are as follows:—

0·5–1 grm. of the well-mixed zinc-dust is weighed in a tube, and poured into a 200 c.c. stoppered flask, the tube being again weighed. For every 0·1 grm. of zinc present, 10 c.c. of a solution of alkali (containing 370 grms. of potassium hydroxide, or 300 grms. of sodium hydroxide per litre), and 3 c.c. of a solution of potassium iodate (containing 15·25 grms. of potassium iodate per 300 c.c.) are measured into a beaker, and then poured into the flask. Some glass beads are added, and the flask stoppered and shaken for five minutes in the cold, no advantage being gained by heating it. Its contents are then washed into a 250 or 500 c.c. flask, and made up to the mark with water. 100 c.c. are now pipetted into the retort of a Topf's apparatus (Fr. 26, 293), dilute sulphuric acid is added, and the apparatus filled with carbon dioxide. A solution of potassium iodide is placed in the receiver, and the retort heated, at first gently, and then more strongly till the contents are perfectly colourless. The stream of carbon dioxide is continued throughout the distillation, which generally occupies about 20 minutes. The solution of iodine in potassium iodide is then transferred from the receiver into a flask, a standard solution of sodium thiosulphate added in slight excess, and the excess titrated back with weak standard iodine solution, starch being used as an indicator. After correcting for the excess, the quantity of zinc is calculated from the amount of thiosulphate used.

Klemp finds that the addition of powdered lead and iron to the zinc makes very little difference in the quantity of zinc found by this process, the results being a little lower in the presence of these metals.

The results by this method agree well with those obtained by Fresenius's method, but are generally higher than those obtained by Drewson's and lower than those obtained by Topf's method (G. Klemp, Fr. 29, 253–266; S. C. I. 9, 968). For a volumetric method, depending on the amount of hydrogen evolved by the action of an acid on zinc-dust, *v.* S. C. I. 5, 145, 1886.

ZINC FLOWERS. Zinc oxide produced by combustion; *v.* Zinc.

ZINC GREEN, *Cobalt green*, or *Rinmann's green*; *v.* Cobalt; also Pigments. This term is also applied to a mixture of zinc yellow and Prussian blue.

ZINC SPAR. Syn. with calamine; *v.* Zinc.

ZINC VITRIOL. *Zinc sulphate v.* Zinc.

ZINC WHITE *v.* Zinc.

ZINC YELLOW, or *Buttercup yellow* and *Zinc chromate*, *v.* Chromium.

ZINKENITE or **ZINCKENITE.** *Lead sulphantimonite v.* Antimony.

ZIRCONIUM. Zr. At.w. 90·4 (Marignac;

Bailey). Zirconium occurs in *zircon* and *hyacinth* as silicate $ZrSiO_4$, in koppite from the Kaiserstühl, and in other rare minerals.

It has been prepared as an amorphous powder and in brittle crystalline scales of sp.gr. 4·15, resembling antimony. The amorphous form burns when gently warmed in air. Zirconium combines with sulphur when heated in a current of hydrogen. It dissolves only in hydrofluoric acid and aqua regia. It belongs to the group of metals containing tin, titanium, and thorium.

Zirconium oxide, zirconia ZrO_2. Powdered zircon is mixed with 3 parts of acid potassium fluoride, and heated in a platinum crucible until free from water. The crucible is placed in a Hessian crucible, and strongly heated in a wind furnace for two hours. The cooled mass is boiled out, the insoluble potassium silicofluoride is filtered off, and the soluble potassium zirconofluoride is crystallised out, heated with sulphuric acid until free from hydrofluoric acid, and dissolved in water, the oxide being precipitated by the addition of cold ammonia. Zirconia has been used to replace lime in the oxy-hydrogen and oxy-coal-gas flame, and, in conjunction with thoria, lanthana, yttria, and other rare earths, for forming the cap of Auer von Welsbach's incandescent gas-burner, these oxides becoming powerfully incandescent in the flame. Zirconia is an acid oxide, and forms *zirconates*.

An oxide of composition Zr_2O_5 has been prepared by G. H. Bailey, and still higher oxides have been obtained by Clève and Bailey. The tetrachloride, tetrabromide, tetriodide, sulphate, and other salts of zirconium are also known.

ZYMURGY. A term used to denote that section of applied chemistry which treats of the scientific principles of those arts in which fermentation is employed—*e.g.* preparation of yeast, vinegar, wine, beer, alcohol.

THE END.

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